THE EFFECT OF STRESS IN CHEMICAL DIFFUSION

by

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We accept this thesis as conforming to the required standard.

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ABSTRACT

Diffusion has been studied in a range of systems having intermediate phases in the diffusion zone. It has been found that in some systems (Ag-Sb, Ag-Se, Ni-Sb, Cu-Se and Cu-Sb) the diffusion rates are very sensitive to compressive stress, with a load of 100 psi making a significant difference to the width of the diffusion zone. In other systems (Cu-Zn, Cu-Sn and Al-Zr) stresses up to the maximum of 1500 psi had no effect on the diffusion rate.

The growth rates of all phases in the pressure sensitive systems were found to be parabolic with time indicating diffusion control. In Cu-Se and Cu-Sb there was a nucleation time at the beginning of diffusion. However, growth of the phases in these systems was also found to be parabolic once this effect was accounted for.

The effect of compressive stress was, generally, to increase the growth rate of one of the intermetallic phases. In Ag-Sb, Ag-Se and Cu-Sb, there was a limiting stress above which growth rates of the intermediate phases were constant. Such a limiting stress was not observed in Ni-Sb and Cu-Se and the growth rates of the Ni$_2$Sb$_2$ and Cu$_2$Se phases in these systems increased apparently linearly with applied stress.

In experiments in which diffusion took place at low stress following an initial high stress anneal, it was generally found that the growth rate characteristic of the new stress was attained after long times of diffusion. In Cu-Se and Cu-Sb however, it was found that the stress-sensitive phases disappeared on ageing, although a finite growth was
observed in the normal growth experiments. From the existing knowledge of diffusion theories, this particular phenomenon could not be explained. However, it is thought that this may possibly be due to a significant decrease in specific volume on formation of these phases.

Non-appearance of certain stable phases predicted from the phase diagram has been attributed to their small diffusion coefficients.

Hydrostatic tests were carried out to see if there was any difference in growth rates between uniaxial compressive stress and triaxial hydrostatic pressure. It was found in general that the growth rate under hydrostatic pressure was very similar to that for a compressive test of zero psi, indicating that applying a hydrostatic pressure does not have any effect on the growth rate and that only compressive loading is of any significance.

All the stress-sensitive systems investigated showed a very large Kirkendall effect. The tungsten markers interfered with diffusion and the width of the diffusion zone adjacent to the markers was less than elsewhere. This gave rise to ledges of the pure metals with the tungsten wires being at the top of the ledges. The development of ledges was much greater in pressure sensitive systems than in other systems and could be attributed to slow lateral diffusion due to the lack of compressive stress in this direction.

The experimental results can be explained on the basis of porosity which forms at a single interface in these systems owing to the large Kirkendall effect. This decreases the effective cross-sectional area of diffusion and so reduces the width of the diffusion zone. The effect of
Compressive stress is to decrease the amount of porosity and hence increase the effective interface area and the atomic flux into the diffusion zone. The limiting stress observed in Ag-Sb, Ag-Se and Cu-Sb was thus attributed to the complete absence of porosity in the diffusion zone. In Ni-Sb and Cu-Se it is believed that the pressure sensitive phases have very high growth rates and the maximum stress of 1500 psi was insufficient to obtain a good interface. All the other results can be explained satisfactorily by the mechanism suggested.
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CHAPTER I
INTRODUCTION

1.1.1 GENERAL

The formation and growth of intermetallic phases in diffusion couples is of considerable significance to metallurgists interested in diffusion bonding, especially in the cladding of fuel elements for nuclear reactors and in the galvanizing and aluminising processes. The strength of the diffusion bonded materials will be dependent on the thickness of the intermediate phases that form during diffusion and on the nature of the interface. Early experiments on the Al-Ni\(^1\) and Al-Fe\(^2\) systems indicated that maximum strength is obtained at an optimum thickness of the diffusion zone and that pressure on the weld can be used to optimise the thickness of the diffusion zone. Observations in Al-U\(^3\) indicated that a non-defective interface can be obtained on application of pressure.

1.1.2 SIGNIFICANCE OF THE STUDY

The widths of the intermediate phases formed during diffusion have been found to be very sensitive to applied pressures sometimes as low as 100 psi. In some systems e.g. Al-Ni\(^1\) and \(\alpha\)-Brass/\(\gamma\)-Brass\(^7\) the thickness of the diffusion zone decreased with increasing pressure whereas in others e.g. Al-U\(^3\), Cu-Sb\(^4,5\) and Cu-Te\(^6\) the width of the diffusion zone increased.

The present investigation was undertaken with a view to determining the generality of the effect of pressure on chemical diffusion and to making a detailed examination of the influence of compressive stress and hydrostatic pressure in those systems which are stress sensitive.
The aim of the investigation was to permit the prediction of the effect of stress on other systems.

1.2 REVIEW OF THE PREVIOUS WORK

Most experiments on the effect of pressure on diffusion have been carried out by pressing a specimen into a die, the specimen being in contact with the die walls to restrict creep, thereby giving semi-hydrostatic conditions.

In the Al-Fe system \(^2\), an increase in the thickness of the diffusion zone with increasing pressure was observed, with, for example, no diffusion being observed below 16,000 psi for a one hour anneal at 525°C whereas at 40,000 psi a zone 55\(\mu\) in width was obtained. (Fig. 1 (a)).

In Ni-Al \(^1,8\), two phases Ni\(_3\)Al\(_2\)(\(\beta\)) and Ni\(_3\)Al\(_2\)(\(\gamma\)) appeared at zero pressure. The thickness of both the phases was progressively reduced with increasing pressure (Fig. 1 (b,c)). According to Storchheim, a pressure of 25,000 psi at 500°C reduced the thickness of the diffusion zone by 50 pct, with the Ni\(_3\)Al phase disappearing between 22,000-40,000 psi and the whole diffusion zone disappearing at 68,000 psi. Castleman and Seigle \(^8\) found that at 600°C the diffusion coefficient of the Ni\(_3\)Al\(_2\) phase decreased by 27 pct on application of a pressure of 10,000 psi; the activation energy increased by 200 cal/mol. Simple calculation shows that the energy required to create one mole of vacant lattice sites in Ni\(_3\)Al\(_2\) under a pressure of 10,000 psi will be approximately 120 cal. Hence the decrease in the thickness of the Ni\(_3\)Al\(_2\) phase with increasing pressure is due mainly to the decrease in the diffusion coefficient in Ni\(_3\)Al\(_2\).
Fig. 1  The effect of pressure on diffusion in Al-Fe and Al-Ni
In α-Brass/γ-Brass couples the thickness of the β-phase formed during diffusion was reduced by 20 pct at a pressure of 20,000 psi. This again has been explained as being due to the decrease of the diffusion coefficient with pressure.

In the Al-U system several investigators have found that the width of the UAl₃ phase increases with pressure. Le Claire and Bear have observed that two phases, UAl₂ and UAl₃, were present in the diffusion zone and that the relative amount of UAl₂ appeared to increase with pressure. This has been contradicted by Castleman who found that only the UAl₃ layer grew to a substantial thickness and that UAl₂ appeared infrequently. A multiphase zone was also observed with no definite boundary. He observed that the rate of formation of UAl₃ at 520°C was 75 pct faster at a pressure of 20,000 psi as compared with a pressure of 2,500 psi. The thickness of UAl₃ approached an asymptotic value as the pressure was increased to 20,000 psi and the diffusion zone became more sound on increasing pressure. It has been suggested that the increase in the width of the diffusion zone is due to the closure of the Kirkendall pores with pressure. This will be discussed in more detail in section 1.4.4.

In Cu-Sb the effect of pressure is greater than in the systems described previously. According to Heumann only one phase, Cu₂Sb(γ), appeared in the diffusion zone at a stress of 495 psi, but above a pressure of 850 psi two phases, Cu₂Sb(γ) and Cu₃Sb(κ), were present. If a diffusion couple containing both Cu₃Sb and Cu₂Sb was annealed at low stress levels the Cu₂Sb grew at the expense of the Cu₃Sb, whereas if a higher pressure was used the reverse phenomenon occurred. This is shown in fig. 2(c). From these measurements they concluded that the Cu₃Sb can grow only above a
Fig. 2  Pressure effect (a) in U-Al, (b) α-Brass/γ-Brass and (c) the effect of changing pressure during diffusion anneal in Cu-Sb
pressure around 570 psi; below this pressure not only was growth impeded but the phase disappeared. They also observed that the Cu$_2$Sb required an incubation period of approximately one hour after which it grew at a much faster rate than Cu$_2$Sb. Heumann gave a tentative explanation of this effect based on the formation of Kirkendall porosity at the diffusion interface.

Diffusion in the Cu-Te system$^6$ showed marked sensitivity to uniaxial compressive stress, with a stress of 20 psi making a significant difference to the width of the diffusion zone. On annealing at 250°C under zero stress, two phases, Cu$_4$Te$_3$ and CuTe, were present in the diffusion zone. The third stable phase, Cu$_2$Te, appeared under compressive loading and its thickness increased apparently linearly with increasing stress. The thickness of the Cu$_4$Te$_3$ appeared to increase with stress up to 400 psi and then decreased whilst the thickness of CuTe decreased progressively with stress. The effects of stress on CuTe and Cu$_4$Te$_3$ were, however, small compared to the effect on Cu$_2$Te. These results are shown in fig. 3 (a). As the pressure varied from 0 to 1,500 psi, the thickness of Cu$_2$Te increased from zero to 86 pct of the total width of the diffusion zone. Growth of the phases Cu$_4$Te$_3$ and CuTe was parabolic with time indicating a volume diffusion controlled mechanism. The results for growth of Cu$_2$Te showed considerable scatter and it was not possible to decide whether growth was controlled by diffusion or by interface reaction (linear growth). Diffusion couples with a wide band of Cu$_2$Te were prepared by diffusing at 250°C at a stress of 500 psi. After 48 hours the load was removed and diffusion was allowed to proceed at zero stress. The results are shown in fig. 3 (b). It is observed that the Cu$_2$Te zone becomes progressively thinner with
Fig. 3 (a) Effect of stress on diffusion in Cu–Te at 250°C and (b) Shrinkage of Cu₄Te₃ at 250°C and zero stress. Original couple was annealed for 48 hrs. at 250°C and 500 psi.
increasing time and disappears within 16 hours, whereas Cu$_4$Te$_3$ and to a lesser extent CuTe grow at the expense of Cu$_2$Te. These experiments show that Cu$_2$Te is not stable at zero stress in a kinetic system. In this case also the effect of stress has been tentatively explained to be due to incipient Kirkendall porosity.

Experiments on Cu-Ag two phase couples by Lindemer and Guy$^{10}$ have shown that diffusion is increased by orders of magnitude when a pressure of 1,000 psi is employed as compared to diffusion under zero pressure. The application of pressure has been shown to produce successful bonding plus diffusion in Al-Zr, Cu-Pt and ternary Cu-Ni-Zr couples under experimental conditions which failed to produce a successful diffusion zone in the absence of pressure.

In summary, two types of systems reacting differently to increasing pressure have been observed. The effect of pressure on Ni-Al$^{1,8}$ and α-Brass/γ-Brass$^7$ which show a decrease in the diffusion zone thickness can be rationalised by considering the decrease in the diffusion coefficient with pressure. The increase in the width of the diffusion zone with pressure in the U-Al$^{3,9}$, Al-Fe$^2$, Cu-Sb$^{4,5}$ and Cu-Te$^6$ systems cannot be rationalised by either changes in diffusion coefficient or changes in the equilibrium concentrations at the phase boundary. The explanation given by most workers is the formation of Kirkendall porosity during diffusion which is affected by the application of pressure in such a manner as to give an apparent increase in the diffusion coefficient.
1.3 THEORY OF DIFFUSION

1.3.1 ATOMIC MECHANISMS FOR DIFFUSION

A variety of mechanisms have been proposed to explain the diffusion process. The interchange mechanism involving correlated rotation of two or more atoms about a common centre is associated with large distortions and does not take place to any extent. The interstitial mechanism involves the motion of an atom from one interstitial site to another and is applicable to systems with open structures and to atoms of small atomic radii. The most probable mechanism for close-packed lattices is the vacancy mechanism, in which atom movement takes place by interchange of vacancy-atom positions. Short-circuit diffusion mechanisms (grain boundary diffusion and dislocation pipe diffusion) are significant only at low temperatures.

On relating the macroscopic diffusion coefficient to the atomic jump mechanism by random walk theory, the following relations are obtained:

\[ D = \alpha \lambda^2 \Gamma \quad \text{(interstitial)} \]
\[ D = \alpha \lambda^2 T N_v \quad \text{(vacancy)} \]

where \( D \) = macroscopic diffusion coefficient.
\( \alpha \) = constant characteristic of the crystal structure.
\( \lambda \) = lattice parameter.
\( \Gamma \) = jump frequency
\( N_v \) = equilibrium vacancy concentration in atom fraction.

Substituting expressions for \( \Gamma \) and \( N_v \) in eq. (1.1) gives:
\[ D = \left[ \frac{1}{6} \lambda \nu \exp \left( \frac{\Delta S_m}{k} \right) \right] \exp \left( - \frac{\Delta H_m}{kT} \right) \]

for interstitial diffusion

\[ D = \left[ \frac{1}{6} \lambda \nu \exp \left( \frac{\Delta S_f + \Delta S_m}{k} \right) \right] \exp \left( - \frac{\Delta H_f + \Delta H_m}{kT} \right) \]

for vacancy diffusion

where \( \nu \) = vibrational frequency of atoms in the crystal.

\( \Delta S_f, \Delta S_m \) = entropies of formation and migration of the defect.

\( \Delta H_f, \Delta H_m \) = enthalpies of formation and migration of the defect.

The term in the square bracket is temperature independent and is generally represented as \( D_0 \).

1.3.2 KIRKENDALL EFFECT

The original experiments of Smigelkas and Kirkendall\(^1\) on marker movement in the Cu/\( \alpha \)-Brass system and further analysis by Darken\(^2\) indicate that different species have different diffusion coefficients and that inert markers move towards that side of the couple with the faster diffusing species. In the Cu/\( \alpha \)-Brass system zinc has a higher diffusion coefficient than copper. Since each atom which moves in one particular direction causes a vacancy to move in the opposite direction, there will be a net flow of vacancies from copper towards brass, equal at any point to the difference between the zinc and copper fluxes. The required net transfer of atoms towards the copper is much greater than could be effected by the number of vacancies which are in thermodynamic equilibrium, so that some sources of vacancies must be operating in the copper. Also the excess vacancies in the brass side must disappear in some way if brass is to shrink and the markers are to move towards the brass side of the couple.
Possible sources of vacancies are grain boundaries, climbing edge dislocations\textsuperscript{16}, moving jogs\textsuperscript{17}. Possible sinks for vacancies are the reversed dislocation movements, formation of faulted dislocation loops and stacking fault tetrahedra by collapse of vacancy clusters, and the formation of pores.

In this thesis most attention will be given to the development of porosity. However, before going on to the details of sources and sinks for vacancies it is necessary to establish the vacancy distribution in the diffusion zone.

1.3.3 VACANCY DISTRIBUTION IN THE DIFFUSION ZONE

The phenomenological model of the Kirkendall effect developed by Darken\textsuperscript{15} and Hartley and Crank\textsuperscript{18}, used widely in diffusion analysis, assumes a) conservation of lattice sites and b) that vacancies are maintained, everywhere, in equilibrium. Observations of porosity in the diffusion zone, deformation markings on the surface of specimens\textsuperscript{19-23} and different rates of marker movement at different points of the couple\textsuperscript{23,24}, all suggest a non-equilibrium vacancy distribution in the diffusion zone. This has been analysed by Seitz\textsuperscript{25,26}, Balluffi and Fara\textsuperscript{27} and recently by Schlipf\textsuperscript{28}.

Balluffi and Fara considered diffusion in a substitutional alloy containing vacancies, and developed equations to represent diffusion of the two substitutional species in terms of the concentration gradient, diffusion coefficients, vacancy life time and the mass flow velocity which was assumed to be due only to sources and sinks for vacancies in different parts of the diffusion zone. Numerical solutions of their equations are
shown in fig. 4 and 5 and were evaluated assuming that essentially a single species was diffusing and that the vacancy life time was small and constant. \( \tau \) is the relative vacancy lifetime and is given by

\[
\tau = \frac{Nvt}{T},
\]

where \( N_v \) = vacancy concentration.

\( t \) = total diffusion time.

\( T \) = vacancy lifetime

and \( R \) is the relative excess vacancy concentration and is given by

\[
R = \frac{N_v}{N_v^0} - 1,
\]

where \( N_v^0 \) = the equilibrium vacancy concentration.

Fig. 4 shows that composition profiles show marked deviation from parabolic behaviour at small \( \tau \) i.e. for small diffusion time (\( t << T \)) but approach the parabolic case as the diffusion time increases. In Fig. 5 it can be seen that the maximum vacancy supersaturation and subsaturation expressed in terms of \( R \) decreases as the diffusion zone widens and diffusion progresses.

1.3.4 KIRKENDALL POROSITY

Fig. 5 shows a region of vacancy supersaturation on that side of the diffusion couple having the faster diffusing species. This vacancy supersaturation can result in the development of pores which move out as diffusion proceeds. Porosity has been found in many systems such as Fe-Ni\(^{29}\), Ag-Au\(^{29}\), Cu-Ni\(^{23,29,30}\), Cu-Al\(^{31,32}\), Ag-Pd\(^{29,30}\), Ni-Au\(^{29,30}\) and Cu/\(\alpha\)-Brass\(^{14,23,31,32}\). The amount of porosity varies from system to system, generally increasing with increasing diffusion time and becoming greater the larger the concentration gradient.
Fig. 4 Diffusion penetration curves as a function of $\lambda$ and $\tau$. (Balluffi and Fara27)

\[ N_1 (\text{Atomic Fraction}) \]

\[ \lambda = X/2\sqrt{Dt} \]

\[ \tau = 0.3 \]
\[ \tau = 1.2 \]
\[ \tau = 4.8 \]

\[ N_1 = 0.15(1 + \text{erf}\lambda) \]

Fig. 5 The relative excess vacancy concentration, $R_\lambda$, as a function of $\lambda$ and $\tau$. (Balluffi and Fara27)
THEORIES OF KIRKENDALL POROSITY

Supersaturation of vacancies leads to the formation of voids. The excess vacancy concentration $N_v$ needed to nucleate a spherical void of radius $'r'$ is given by the Gibbs-Thomson relation

$$\ln \frac{N_v}{N_v^0} = \frac{2s}{NkT}$$  \hspace{1cm} (1.3)

where $N_v^0$ = equilibrium vacancy concentration.

$k$ = Boltzmann's constant.

$T$ = absolute temperature.

$s$ = surface energy.

$N$ = atomic density.

Vacancies may condense to form voids in a perfect lattice if $\frac{N_v}{N_v^0}$ is of the order of 100 or greater\textsuperscript{33} if a critical radius of $10^{-3}$ cm is assumed for the nuclei. This number is very high and homogeneous nucleation rarely takes place.

The supersaturation necessary will be much less if heterogeneous nucleation is considered, the nucleation sites being small voids, cracks and foreign particles (observed in Cu/$\alpha$-Brass\textsuperscript{35,36} and Cu-Ni\textsuperscript{36}). Balluffi\textsuperscript{37} has shown that a maximum vacancy supersaturation of only 1 pct is necessary for the heterogeneous nucleation of voids, in agreement with the experimental results in Cu-Ni\textsuperscript{36}. Assuming 1 pct vacancy supersaturation, Seitz has shown that nuclei of radius of the order of 1,000 atomic distances will be effective for the growth of voids. He has also concluded from the results of Barnes\textsuperscript{23} and Bückle and Blin\textsuperscript{32} that between a third and a half of the vacancy current is transferred to pores and this has been observed in Cu/$\alpha$-Brass\textsuperscript{34}. 
Brinkman\textsuperscript{19} has taken into account the possibility of a change in the potential energy in the region around a void upon absorption of a vacancy when a stress field is present. He has shown that a stress equivalent to the yield stress of the material will develop in the diffusion zone if it is assumed that only 1 pct of the vacancies are interacting with dislocations. In the presence of a stress field \( F \) the Gibbs-Thomson equation is given by\textsuperscript{19}

\[
\ln \frac{N_v}{N_v^0} = \left[ \frac{2s}{r} - \frac{3F}{4(\lambda + 2\mu)} (3F - \frac{4s}{r}) \right] /NkT
\]

(1.4)

where \( \lambda \) and \( \mu \) are Lame's constants.

If \( F \) is taken to be of the order of \( 1.5 \times 10^4 \) psi, this quantity changes sign when \( r = 10^{-3} \) cm. for Cu. Thus, once nuclei of this size are formed, no excess vacancy concentration is necessary for their growth if a stress field of sufficient strength is present. Brinkman\textsuperscript{19} suggests that these nuclei may form by a process of fissuring at the interface between the portion of the diffusion zone undergoing plastic deformation under the stress field and the region outside the diffusion zone which is free of stress.

Porosity formed during the diffusion process can act as an obstruction to diffusion by decreasing the cross-sectional area, particularly when a substantial fraction of the area is covered by voids. This is important in the present work and will be discussed in more detail in a later section.
1.3.5 **MATHEMATICS OF DIFFUSION**

Fick's first law is given by

\[ J = -D \frac{\delta c}{\delta x} \]  

(1.5)

where \( J \) = flux/unit volume/unit time.

\( D \) = diffusion coefficient

\( \frac{\delta c}{\delta x} \) = concentration gradient.

Fick's second law is given by

\[ \frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left( D \frac{\delta c}{\delta x} \right) \]  

(1.6)

For the semi-infinite single phase diffusion couple shown in fig. 6 (a), eq. (1.6) can be transformed to give a diffusion equation in a single variable, \( \lambda = \frac{x}{\sqrt{D}} \). This can then be integrated twice assuming \( D \) to be constant to give the solution,

\[ \frac{c - c_0}{c_1 - c_0} = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{\lambda}{2\sqrt{D}} \right) \right] \]  

(1.7)

where \( \text{erf} \left( \frac{\lambda}{2\sqrt{D}} \right) \) is the Gaussian error function defined by \( \text{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\eta^2} \, d\eta \).

In systems with miscibility gaps between the various stable phases, discontinuities occur in the concentration vs distance profile across the two phase regions, as shown in fig. 6 (b). Diffusion within the various phases is quite normal and as in single phase systems, the profile can be drawn in \( \lambda \)-space to eliminate \( x \) and \( t \) as independent variables. This means that the phase boundaries or discontinuities occur at constant values for \( \lambda \) and so the motion of the phase boundary is parabolic with time.

If it can be assumed that the diffusion coefficient in an intermetallic phase is independent of concentration, then the composition
**Fig. 6** Schematic representation of diffusion profile (a) for a system with complete solid solubility (b) for a system having one intermediate phase.
profile in that phase is a portion of an error function. For the simple case where there is no solid solution in the terminal phases, the profile shown in fig. 6 (b) is given by:

\[
c = \left[ \frac{c_{YB} \text{erf} \frac{a_1}{2\sqrt{D}} - c_{YA} \text{erf} \frac{a_2}{2\sqrt{D}}}{\text{erf} \frac{a_1}{2\sqrt{D}} - \text{erf} \frac{a_2}{2\sqrt{D}}} \right] + \left[ \frac{c_{YA} - c_{YB}}{\text{erf} \frac{a_1}{2\sqrt{D}} - \text{erf} \frac{a_2}{2\sqrt{D}}} \right] \text{erf} \frac{\lambda}{2\sqrt{D}} \quad (1.8)
\]

where \(a_1\) and \(a_2\) are the growth constants at the A/\(\gamma\) and \(\gamma/B\) interfaces respectively and \(D\) is the diffusion coefficient of the \(\gamma\)-phase.

By considering the mass balance across the phase interfaces i.e. taking the motion of phase boundary to be controlled by the flux down the concentration gradient, values of \(a_1\) and \(a_2\) are given by:

\[
(c_A - c_{YA}) \frac{\sqrt{\pi}}{2} a_1 = \frac{(c_{YA} - c_{YB})^{\frac{1}{2}} \exp (-\frac{a_1^2}{4D})}{\text{erf} \frac{a_1}{2\sqrt{D}} - \text{erf} \frac{a_2}{2\sqrt{D}}}
\]

and

\[
(c_{YB} - c_B) \frac{\sqrt{\pi}}{2} a_2 = -\frac{(c_{YA} - c_{YB})^{\frac{1}{2}} \exp (-\frac{a_2^2}{4D})}{\text{erf} \frac{a_1}{2\sqrt{D}} - \text{erf} \frac{a_2}{2\sqrt{D}}}
\]

In the case where the intermetallic compound occurs at 50 at pct and has an equal composition range on either side of stoichiometry i.e. \(c_{YB} - c_B = c_A - c_{YA}\), \(a_2 = -a_1 = \alpha\) and \(c_B = 0\), eq. (1.9) can be written as:

\[
(c_{YB})^{\frac{1}{2}} \alpha = \frac{(c_{YA} - c_{YB})^{\frac{1}{2}} \exp (-\frac{\alpha^2}{4D})}{2 \text{erf} \frac{\alpha}{2\sqrt{D}}}
\]

(1.10)
Eq. (1.10) shows clearly that as the composition range of the intermetallic compound tends to zero, the growth rate of the phase will become very small.

The analysis obtained above can be extended to cases where more than one intermetallic phase appears in the diffusion zone. Growth of all phases will be parabolic with time if diffusion controlled with the growth rate of any intermediate phase depending on factors such as the diffusion coefficient within the phase and in the adjoining phases, the homogeneity range of the phase and the concentration range of the adjacent two phase regions. Baird\textsuperscript{38} has suggested that in intermetallic compounds with a very low homogeneity range, large growth rates are possible because of the thermodynamic factors which give extremely large diffusion coefficients within the phases.

In systems showing only one intermetallic phase and no solid solubility the growth rate is given by\textsuperscript{39}

$$a_1^2 = \frac{2D (c_2 - c_1)(c_3 - c_2)}{(c_1 - c_0)(c_3 - c_2 + c_1 - c_0)}$$

if a linear concentration profile within the phase is assumed as shown in fig. 7 (a).

![Fig. 7](image-url)

**Fig. 7** Schematic composition profiles for two cases of intermetallic diffusion
The same analysis can be extended to systems showing more than one intermetallic phase and no solid solubility. Assuming a linear concentration gradient within the phases, the concentration gradients in phases 1 and 2 are given by:

\[
\frac{\delta c}{\delta x} = \frac{c_4 - c_3}{\xi_2 - \xi_3} \quad (1.12)
\]

and

\[
\frac{\delta c}{\delta x} = \frac{c_2 - c_1}{\xi_1 - \xi_2}
\]

Considering the mass balance at \( \xi_3 \) gives

\[
(c_5 - c_4) \frac{d\xi_3}{dt} = -D_1 \frac{\delta c}{\delta x} = -D_1 \frac{c_4 - c_3}{\xi_2 - \xi_3}
\]

and hence

\[
\alpha_3(\alpha_2 - \alpha_3) = -2D_1 \frac{c_4 - c_3}{c_5 - c_4}
\]

since \( \xi_1 = \frac{\alpha_1}{\sqrt{t}} \), \( \xi_2 = \frac{\alpha_2}{\sqrt{t}} \) and \( \xi_3 = \frac{\alpha_3}{\sqrt{t}} \)

Similarly, the mass balance at \( \xi_1 \) gives

\[
\alpha_1(\alpha_1 - \alpha_2) = 2D_2 \frac{c_2 - c_1}{c_1 - c_0}
\]

\( \alpha_1 \), \( \alpha_2 \) and \( \alpha_3 \) can be found by determining the Matano interface in the composition profile and the diffusion coefficients in the phases can be calculated from eqs. (1.13) and (1.14).

1.3.6 DIFFUSION IN IONIC COMPOUNDS

In multiphase diffusion involving growth of ionic compounds, the kinetics of the process will be controlled either by diffusion of ions through the intermediate phase or by phase boundary reactions including transport through the space charged boundary layer.

Diffusion in ionic crystals takes place by the movement of defects. In ionic crystals, deviation from stoichiometry takes place by
the formation of cation vacancies or interstitials, or anion vacancies. To maintain electrical neutrality similar number$ of electrons or holes must be formed. Diffusion in non-stoichiometric compounds takes place by a movement of ions which is always coupled with a flow of electrons or holes to maintain electrical neutrality at every point in the diffusion zone. Electrons can diffuse much faster than ions but are constrained to move in step with the ions and merely have the effect of doubling or tripling the ion diffusion coefficient.

The nature of the diffusing species can be determined by Kirkendall marker experiments. For example, in Ag$_2$S silver ions are the diffusing species$^4$. Silver atoms ionize at the Ag/Ag$_2$S boundary to give Ag$^+$ ions plus electrons. These diffuse through the Ag$_2$S phase to the Ag$_2$S/S boundary where chemical reaction takes place to form Ag$_2$S and thus give rise to an increase in the thickness of the diffusion zone. Since Ag$^+$ ions are diffusing in Ag$_2$S, Kirkendall markers will remain at the Ag/Ag$_2$S interface.
1.4 EFFECT OF PRESSURE ON MULTIPHASE DIFFUSION

1.4.1 POSSIBLE EFFECTS

Pressure or uniaxial stress can affect the width of the diffusion zone by one or more of the following processes:

a) Alteration of the diffusion coefficient.

b)Alteration of the equilibrium compositions of the phases.

c) Changing the conditions for the formation of Kirkendall porosity thereby affecting the diffusion kinetics of the system.

The relative significance of each of these processes will be discussed in turn.

1.4.2 EFFECT OF PRESSURE ON DIFFUSION COEFFICIENT

The effect of hydrostatic pressure on diffusion has been the subject of increasing attention during the past decade\(^{42,43}\). It is now well established that the self diffusion coefficient of an element is reduced by hydrostatic pressure\(^{44,45}\) and that the anisotropy of the self diffusion coefficient is reduced in non-cubic metals such as zinc\(^{46}\).

The diffusion coefficient, \(D\), is given by eq. (1.1) and (1.2) in page 10. The effect of pressure on \(D\) will be a combined effect on the equilibrium defect concentration and on the jump frequency. Taking logarithms of eq. (1.2) and differentiating with respect to pressure gives:
The terms in \( D_0 \) (i.e. \( \nu \), \( \lambda \), \( \Delta S_m \), \( \Delta S_f \)) do not vary with pressure unless high pressures are used and hence

\[
\frac{\delta \ln D}{\delta P} = 0
\]
TABLE I

D(P)/D(o) FOR VARIOUS MATERIALS AT T/Tm = 0.5 AND P = 10,000 psi

<table>
<thead>
<tr>
<th>Material</th>
<th>( V_Q ) in ( \text{A}^3 )/atom</th>
<th>( T_m ) in °K</th>
<th>( T ) in °K</th>
<th>( \frac{D(P)}{D(o)} ) in pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>15.2(^{47})</td>
<td>1233.5</td>
<td>611.75</td>
<td>88.4</td>
</tr>
<tr>
<td>Pb</td>
<td>21.6(^{48})</td>
<td>610.4</td>
<td>305.2</td>
<td>70.3</td>
</tr>
<tr>
<td>Ag-Zn(27 pct)</td>
<td>8.9(^{49}) (solidus)</td>
<td>1023.0</td>
<td>511.5</td>
<td>91.6</td>
</tr>
<tr>
<td>Li</td>
<td>6.0(^{50})</td>
<td>553.0</td>
<td>276.5</td>
<td>89.7</td>
</tr>
<tr>
<td>Na</td>
<td>20.5(^{44})</td>
<td>370.6</td>
<td>185.3</td>
<td>57.6</td>
</tr>
<tr>
<td>P(white)</td>
<td>49.8(^{43})</td>
<td>317.4</td>
<td>158.7</td>
<td>20.9</td>
</tr>
</tbody>
</table>
pressure on diffusion rates is much higher. Values of \( \frac{D(P)}{D(o)} \) have been calculated at 10,000 psi at \( T/Tm = 0.5 \) and are shown in Table 1. All the experiments described above refer to tracer self-diffusion. No work has been carried out on the effect of pressure on the chemical diffusion. However, it is believed that effects of similar magnitude to self diffusion would be observed.

**1.4.3 EFFECT OF PRESSURE ON EQUILIBRIUM COMPOSITION**

Pressure can affect the diffusion characteristics in multiphase systems by changing the composition range or the stability of the phases, thereby changing the diffusion profile of the system. Extensive research has been carried out on the effect of pressure on the temperature of polymorphic transformation and melting point of pure metals. On the other hand research on phase equilibria in multicomponent system has been very limited\(^{51,52}\).

The effect of pressure on the phase diagram depends on the molar volumes of the intermetallic phases and the terminal phases. A schematic representation of the effect of pressure on phase equilibria is given in fig. 9 (a). The \( \alpha, \gamma \) and \( \beta \) phases are in thermodynamic equilibrium at temperature \( T \) in fig. 9 (b). In case 1, where \( V_\gamma > V_\alpha > V_\beta \), application of pressure increases the composition range of the \( \beta \)-phase and decreases that of the \( \gamma \)-phase. In case 2, where \( V_\alpha > V_\beta > V_\gamma \), the composition range of \( \gamma \) increases whereas that of \( \alpha \) is decreased. In general, it is observed that pressure increases the field of stability of the phase with lower molar volume. This concept can be developed quantitatively by thermodynamic analysis\(^{51,52}\) as follows:
Free energy diagrams at temp. 'T' showing variation of composition with pressure when the specific volumes are differently related. $V_\gamma$, $V_\alpha$, and $V_\beta$ are the molar volumes of the $\alpha$, $\beta$, and $\gamma$ phases respectively.

**Fig. 9** Free energy diagrams at temp. 'T' showing variation of composition with pressure when the specific volumes are differently related. $V_\gamma$, $V_\alpha$, and $V_\beta$ are the molar volumes of the $\alpha$, $\beta$, and $\gamma$ phases respectively.

(a) $V_\beta > V_\gamma > V_\alpha$

(b) $V_\gamma > V_\alpha > V_\beta$ (case 1)

(c) $V_\alpha > V_\beta > V_\gamma$ (case 2)
In binary systems the boundaries and critical points for two and	hree phase equilibria can be described mathematically by relationships
obtained by equating the chemical potentials or partial molar free energies
of both components at the phase boundaries i.e. (refer to the \( \alpha/\gamma \) phase
boundary in fig. 9 (b)).

\[
\frac{\delta F}{\delta c} = \frac{\delta F}{\delta c} = \frac{\delta F}{\delta c}
\]

where \( F = F(c) \) and \( \frac{\delta F}{\delta c} \) is the partial molar free energy
of the alloy at composition \( c \).

Equation (1.17) can be differentiated with respect to pressure,
and using eq. (1.18) the change in equilibrium composition with pressure can
be formulated and is given by:

\[
\frac{dc_{\gamma\alpha}}{dP} = - \left( \frac{\Delta V}{\alpha} - \frac{\Delta V}{\alpha\gamma} \right) \cdot \frac{\delta F}{\delta c}
\]

where \( \Delta V \) is the difference in the molar volumes of the \( \alpha \)-phase and the \( \gamma \)-phase. If suitable thermodynamic and
cumetric data are available eq. (1.19) can be integrated to obtain \( c_{\gamma\alpha}(T,P) \).
In the special case where there is no terminal solid solution and in which the \( \gamma \)-phase has a low range of composition on either side of 50 at pct, eq. (1.19) can be modified to give:

\[
\frac{dc_{\gamma\alpha}}{dP} = -\frac{(1 - 2c_{\gamma\alpha})(1 - c_{\gamma\alpha})}{RT c_{\gamma\alpha}} \left[ V_A - \frac{V_A}{c_{\gamma\alpha}} \right] \\
\frac{dc_{\gamma\beta}}{dP} = \frac{(2c_{\gamma\beta} - 1)c_{\gamma\beta}}{RT (1 - c_{\gamma\beta})} \left[ V_B - \frac{V_B}{c_{\gamma\beta}} \right]
\]

(1.20)

\( V_A, V_B \) = molar volumes of A and B respectively

It is important to note that the effect of pressure on equilibrium composition is characterised by the molar volumes of the phases in equilibrium. Thus the compositional field of the \( \gamma \)-phase will expand with pressure if \( \frac{dc_{\gamma\alpha}}{dP} \) is negative and \( \frac{dc_{\gamma\beta}}{dP} \) is positive and hence depends on the sum of the volumetric terms in eq. (1.20) being positive. In iron-base alloys which show a \( \gamma \)-loop, hydrostatic pressure expands the \( \gamma \)-loop by increasing the stability of the denser f.c.c. phase at the expense of the less dense b.c.c. \( \alpha \)-phase.\(^{51-58}\)

1.4.4 RELATIVE SIGNIFICANCE OF EFFECT OF PRESSURE ON DIFFUSION COEFFICIENT AND PHASE BOUNDARY COMPOSITION

Castleman\(^{59}\) has discussed the relative importance of changes in diffusion coefficient and changes in phase boundary composition in systems showing an intermediate phase (\( \gamma \)) and no solid solubility. The diffusion profile is given by eq. (1.10) in page 18.
Differentiating eq. (1.10) with respect to pressure and rearranging gives:

\[ \frac{1}{a} \frac{d\alpha}{dp} = \frac{1}{2} \left( \frac{1}{D} \frac{dD}{dp} \right) + \mu \left( \frac{1}{c_{\gamma A}} \frac{dc_{\gamma A}}{dp} - \frac{1}{c_{\gamma B}} \frac{dc_{\gamma B}}{dp} \right) \]  

(1.21)

where \( \mu = \frac{c_{\gamma A}}{c_{\gamma A} \left(1 + \frac{\alpha^2}{2D}\right) - c_{\gamma B} \left(1 - \frac{\alpha^2}{2D}\right)} \)  

(1.22)

Equation (1.21) implies that a value of \( \mu > \frac{1}{2} \) will cause pressure induced concentration changes to outweigh any effect resulting from pressure induced diffusivity changes on the growth kinetics of the intermediate phase; if \( \mu < \frac{1}{2} \) the situation is reversed.

Castleman has calculated the change in composition with hydrostatic pressures up to 7.4 x 10^5 psi using a simplified version of eq. (1.19) [page 27], with the assumptions that the free energy curves are essentially parts of circles and that the shapes of these curves do not change with pressure, being merely raised to higher values on application of pressure. His calculations show that the shifts in composition are very small and do not exceed 0.1 pct of the original value unless a pressure induced free energy increase of over 600 cal/g atom (25,000 cm^3 atm.) is postulated i.e. a molar volume change of 5cc is assumed which is very high for the systems studied. Using these values, calculating the factor '\( \mu \)' and determining \( \frac{1}{a} \frac{d\alpha}{dp} \) from experiment, one can calculate the contribution of the change in the diffusion coefficient to the growth rate. Castleman has calculated these factors and found that for the Ni-Al system \( \frac{\Delta D}{D} \) is negative indicating a decrease in the diffusion coefficient and that the contribution from this factor is much higher than that due to concentration...
changes with pressure. Hence he rationalises the decrease in the thickness of the Ni$_2$Al$_3$ layer with pressure to be due to a decrease in the diffusion coefficient. However, in U-Al in which the width of the UAl$_3$ layer increases with pressure, a similar calculation suggests a positive $\frac{AD}{D}$ indicating an apparent increase in the diffusion coefficient, the term due to concentration changes being negligible. This is in contradiction with the observation that the diffusion coefficient generally decreases with increasing pressure. An alternative explanation of the pressure effect in U-Al will be discussed in the next section.

The effect of pressure on the diffusion coefficient is approximately one order of magnitude greater than the effect due to the equilibrium concentration change. Consequently a pressure induced change in interfacial concentration is not important unless the function $\nu$ is at least greater than five and probably greater than fifty. It may, therefore, be concluded that the main effect of pressure will be due to apparent variations of the diffusion coefficient.

1.4.5 EFFECT OF PRESSURE ON KIRKENDALL POROSITY

The third possible factor that may be sensitive to pressure is the Kirkendall porosity. Study of the Kirkendall effect under hydrostatic pressures of large magnitude ($7.7 \times 10^5$ psi) in In-Tl and Fe-V did not show any porosity in the diffusion zone. Geguzin has observed that the amount of Kirkendall porosity decreases with increasing pressure - in the Cu/o-Brass system porosity completely disappeared above 145 psi and in the Cu-Ni system no porosity was observed above 1420 psi. Barnes and Mazey have studied the effect of pressure in the Cu-Ni system in detail. They
observed that a hydrostatic pressure of 1300 psi at 1000°C prevents the formation of voids, and that a pressure of 2300 psi eliminates voids previously formed by a 4 hour 1000°C anneal in vacuo. The large difference in these two pressures indicates that the pressure of 1300 psi does not merely collapse voids which form early in the anneal. The voids retained an approximately spherical shape during their regression suggesting that the collapse was by a diffusional process rather than a deformation process. They explain their results by assuming a hydrostatic stress condition and introducing a term PV in the Gibbs-Thomson equation (eq. (1.3) on page 14), PV being the extra work done in forming a void of volume V against the external pressure P. Hence, eq. (1.3) is modified to

$$kTN \ln \frac{N_v}{N_v^0} = \frac{2S}{r} + P \quad (1.23)$$

Their calculations indicate that the critical radii in the Cu-Ni system are,

$$r_c (1300 \text{ psi}) = 2.8 \times 10^{-5} \text{ cm.}$$
$$r_c (0 \text{ psi}) = 1.2 \times 10^{-5} \text{ cm.}$$

Hence, nucleation of pores at high pressures is more difficult than at low pressures.

The porosity developed in single phase systems can be quite extensive if there is a significant difference in the diffusion rates of the two species. In Ag-Au, for example, approximately 40 ppt of the cross-sectional area of the diffusion couple is taken up by pores. This extensive porosity can significantly hinder diffusion and lead to a noticeable decrease in the width of the diffusion zone.
In multiphase systems the effect can be much greater, since in some intermetallic compounds essentially only one component is diffusing. This means that the necessary vacancy flux has the same magnitude as the diffusion flux and also that the vacancies will condense out at one plane in the diffusion zone. Hence in such systems there will be a strong tendency for porosity to interfere with the diffusion flux. Application of an external pressure to the system will prevent pores being formed and so give a wider diffusion zone. The stresses required for this are expected to be comparable to those in a single phase system and would generally be less than 2500 psi.

This explanation has been used to explain the results on systems like Cu-Sb\textsuperscript{4,5}, Cu-Te\textsuperscript{6} and U-Al\textsuperscript{3} already discussed in pages 4-6. All these systems have a large Kirkendall effect and so will have the large vacancy flux necessary to develop extensive porosity. If this explanation is correct, one would expect the pressure induced increase in layer growth to disappear once the pressure is sufficiently great to eliminate the macroscopic defects.
CHAPTER II

EXPERIMENTAL

2.1 CHOICE OF SYSTEMS

The object of this work was to study the effect of stress on multiphase diffusion in a range of systems. The systems selected for this study were determined by the following factors.

1. Materials undergoing rapid oxidation are difficult to handle in the apparatus used

2. Systems should be such as to yield a measurable diffusion zone at relatively low temperatures

3. The materials should not creep in the course of a diffusion anneal.

The systems studied were Cu-Zn, Cu-Sn, Zn-Se, Zn-Sb, Ag-Te, Al-Zr, Ag-Sb, Ag-Se, Ni-Sb, Cu-Sb, and Cu-Se.

2.2 APPARATUS

The apparatus used for preparing diffusion couples under an applied stress is shown in fig. 10. A uniaxial compressive load was applied to the system through a simple lever bar. A stainless steel (316) rod activated by a lever arm lay inside a stainless steel tube. The diffusion couple lay on top of the steel rod in a specimen holder and stress was applied to the couple between the rod and a plug welded into the centre of the tube. To ensure a uniform stress across the couple a hemispherical boss and cup were used to transmit the load to the diffusion couple. A 400 w. tube furnace with a uniform hot zone 3" long slid around the stainless steel tube, and maintained the assembly
Fig. 10  Apparatus for carrying out diffusion under compressive Stress
at the desired temperature. A thermocouple situated 1/2" from the specimen operated a proportional temperature controller which maintained the specimen temperature constant to ± 2°C. A clearance of 1/16" between the specimen holder and the specimen was maintained to ensure a uniaxial compressive load. The pressure applied had a reproducibility of ± 10 psi, the main source of error being in the measurement of specimen dimensions. Error due to friction was avoided in the design of the apparatus.

The apparatus was designed to be used at 600°C with a stress of up to 10,000 psi. The lever bar was calibrated for a specimen size of 0.5" in diameter.

2.3 MATERIALS AND SPECIMEN PREPARATION

The materials used were supplied by Western Alloys and Metals Ltd. (Cu), Cominco (Ag and Zn), International Nickel Company (Ni), Wah-Chang Corp. (Zr), Fairmount Chemical Co. Inc. (Sb and Se), Vulcan Detinning div. (Sn) and were of the following purity:

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.92 pct.</td>
</tr>
<tr>
<td>Ag</td>
<td>99.95 pct.</td>
</tr>
<tr>
<td>Ni</td>
<td>99.92 pct.</td>
</tr>
<tr>
<td>Sb</td>
<td>99.8 pct.</td>
</tr>
<tr>
<td>Se</td>
<td>99.99 pct.</td>
</tr>
<tr>
<td>Zn</td>
<td>99.99 pct.</td>
</tr>
<tr>
<td>Zr</td>
<td>99.99 pct.</td>
</tr>
<tr>
<td>Sn</td>
<td>99.95 pct.</td>
</tr>
</tbody>
</table>

Copper, silver, and zirconium discs were cut from bar stock whereas nickel specimens were spark-machined from nickel plates. Zinc and tin specimens were cut from cast bars. Antimony was melted in a plumbago crucible at 675°C and cast into preheated (600°C) graphite slab
moulds to give a flat slab of 6" x 1" x 1/4" dimensions. The slabs were annealed at 500°C for 8 hrs. and 0.5" diameter specimens were spark-machined from the slabs. Selenium was also melted in a plumbago crucible at 250°C and cast into 0.5" dia. bars in a pyrex glass mould. On solidification the selenium had a glassy structure and was amorphous. This could not be used for diffusion experiments since it crept badly at 50°C and 100 psi. The cast bars in glass moulds were, therefore, heat treated at 200°C for 2-3 hrs to obtain the crystalline form of selenium. Specimens were then cut from the bars with a jeweller's saw.

2.4 EXPERIMENTAL PROCEDURE

Specimens 0.5" in diameter by approximately 1/4" in thickness were ground flat to 3/0 emery paper, and washed in soap, water and acetone. Ultrasonic cleaning was used for a final cleaning step in initial experiments but was omitted in later experiments since it did not affect the width of the diffusion zone. The specimens were inserted and removed from the pressure apparatus with the furnace at operating temperature. It took the specimens only 2 minutes to reach diffusion temperature - a time small compared with the diffusion times. Stress was applied immediately after the specimens were introduced. All diffusion experiments were carried out in a hydrogen atmosphere. Following the diffusion anneal, the specimens were mounted in cold mount and ground on a belt grinder so that a section through the diameter was being examined. The section was then ground to 3/0 emery paper, polished and etched.
The following etchants were used:

<table>
<thead>
<tr>
<th>Etchants</th>
<th>Cu-Sb</th>
<th>Cu-Se</th>
<th>Ag-Sb</th>
<th>Ag-Se</th>
<th>Ni-Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂Cr₂O₇</td>
<td>2 gm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ (conc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂Cr₂O₇</td>
<td>6 gm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl(sat. soln)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromic Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl(Conc)</td>
<td>2 cc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The phase layers were measured using a Filar eye-piece with 10-15 readings being taken for each specimen and the average thickness being calculated. About half the experiments were repeated and the reproducibility was always found to be within ± 20μ. The average value was used for plotting the graphs.

The phases in the diffusion zone were identified by both electron probe analysis and x-ray diffraction.

Specimens were prepared for electron probe analysis by polishing with 1μ diamond paste. An electrostatically focused electron
probe with a take-off angle of 12-deg and a spot diameter of less than 10μ was used. Values of X-ray intensity were converted to weight percent using the matrix absorption correction method of Castaing and Descamps and the fluorescent correction procedure of Birks.

For X-ray determination of d-spacings for the intermetallics, specimens with a thick diffusion zone were broken and the intermetallic layers were filed to give a fine powder. Care was taken not to mix the phases when more than one phase was present in the diffusion zone. A diffractometer trace of the powder was made using a Norelco X-ray diffractometer with Cu-Kα radiation. The 2θ values corresponding to the diffraction peaks were compared with standard ASTM cards to identify the phases.

To investigate the Kirkendall effect, diffusion couples were prepared with 0.001" tungsten wire markers in the diffusion zone. The wires were pressed into the ductile part of the sample (Cu, Ag, Ni) and the surface ground on 3/0 emery paper prior to assembling in order to give completely flat interfaces.

Hydrostatic tests were carried out in a steel pressure vessel connected to a hydrogen gas cylinder by a pressure tube. The specimens were prebonded under compressive stress and were then inserted into the pressure vessel containing Dow Corning F-1-0173 silicone oil. The pressure transmitting tube was screwed on tightly to the pressure vessel which was then inserted into the furnace. The required temperature was attained within 10 minutes and the required pressure was applied by a regulator. The assembly is shown in fig. 11.
Stainless Steel Pressure Tube

Furnace
Copper washer to maintain pressure
Stainless Steel pressure vessel with Silicone Oil specimen

Stainless Steel Furnace Tube

Bench

To $\text{H}_2$ gas
Cylinder with pressure gauge

Fig. 11 Apparatus for Hydrostatic Experiments
3.1. PRELIMINARY STUDIES

Initial studies on the Cu-Zn, Cu-Sn and Al-Zr systems did not show any effect of stress over the range of 0-1500 psi. The Zn-Se and Zn-Sb systems did not give a uniform diffusion zone - the intermetallic compound formed only on certain grains of zinc indicating a possible orientation dependence. In Ag-Te, significant grain boundary diffusion made measurements of the diffusion zone difficult. A marked stress sensitivity, however, was observed in Ag-Te, Zn-Sb and Zn-Se, although it was not possible to study it quantitatively because of the nature of the diffusion zones. Extensive work was carried out in Ag-Sb, Ag-Se, Ni-Sb, Cu-Se and Cu-Sb. These systems showed a uniform diffusion zone consisting of one or more intermetallic compounds. The results on Ag-Sb and Ag-Se will be presented first in this chapter, since these systems showed only one intermetallic compound. These will be followed by results in Ni-Sb, Cu-Se and Cu-Sb which had two or three phases in the diffusion zone.

3.2 SILVER - ANTIMONY SYSTEM

3.2.1 THE PHASE DIAGRAM

The phase diagram of the Ag-Sb system is shown in fig. 12. It is observed that there is only slight solubility of antimony in silver and no solid solubility of silver in antimony. There are two stable intermediate phases - $\zeta$ (8.8 - 16.3 wt % Sb) and $\text{Ag}_3\text{Sb}$ (23 - 27 wt % Sb). The $\zeta$-phase, stable below 702°C, is a 3/2 electron compound having an h.c.p. structure with $a = 2.955\text{Å}$ and $c = 4.788\text{Å}$. The $\text{Ag}_3\text{Sb}$ phase, stable below 558°C,
Fig. 12  Phase diagram of the Ag-Sb system (Hansen 70)
a 7/4 electron compound having an orthorhombic\textsuperscript{67} (Cu\textsubscript{3}Ti type) structure with \(a = 5.99\text{\AA}^0\), \(b = 5.24\text{\AA}^0\) and \(c = 4.85\text{\AA}^0\).

Specific volumes, defined as the volume of one gram of the material, were calculated for both stable phases from density or lattice parameters obtained from the literature and are shown in table 2. It is observed that silver and antimony undergo a contraction of 6.1 pct when reacting to form the Ag\textsubscript{3}Sb phase and a very slight expansion (0.4 pct) when forming the \(\zeta\)-phase. This would suggest that application of pressure would facilitate the formation of Ag\textsubscript{3}Sb over the \(\zeta\)-phase.

3.2.2 IDENTIFICATION OF THE PHASE

Diffusion couples of Ag-Sb annealed at 350\degree C and 400\degree C produced very uniform diffusion zones containing only one intermediate phase. The phase was identified by electron probe microanalysis and by X-ray diffraction as Ag\textsubscript{3}Sb. The probe traverse is shown in fig. 13 and the X-ray data are given in Appendix 1. There appeared to be no concentration gradient within the intermetallic phase and no terminal solid solubility could be observed in the silver or in the antimony. According to the phase diagram silver can take up to 6.5 pct Sb in solid solution at 350\degree C. However the solid solution diffusion rate of antimony in silver at this temperature will be very small compared with the diffusion rate in the Ag\textsubscript{3}Sb. Hence there will be some solid solubility of antimony in silver, but the diffusion distance will be so small it will not appear in the probe traverse. The second phase (\(\zeta\)) was not observed in any of the diffusion experiments.
### TABLE 2

**SPECIFIC VOLUMES OF INTERMEDIATE PHASES IN Ag−Sb**

<table>
<thead>
<tr>
<th>Phase</th>
<th>ζ-phase</th>
<th>Ag$_3$Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Volume of Ag reacting to form 1 g. of the compound</td>
<td>0.07152 cc.</td>
<td>0.07152</td>
</tr>
<tr>
<td>2. Volume of Sb reacting to form 1 g. of the compound</td>
<td>0.02875 cc.</td>
<td>0.03776</td>
</tr>
<tr>
<td>3. Total volume of Ag and Sb reactant.</td>
<td>0.10027 cc.</td>
<td>0.1093</td>
</tr>
<tr>
<td>4. Specific volume of the phase</td>
<td>0.09982 cc/gm</td>
<td>0.1026$^{69}$</td>
</tr>
<tr>
<td>5. Net change in the volume during reaction (pct.)</td>
<td>-0.43%</td>
<td>-6.11%</td>
</tr>
</tbody>
</table>
**Fig. 13** Electron probe traverse of Ag-Sb diffusion couple aged for 25 hrs. at 350°C and 300 psi. Probe traverse made using Sb - Lα radiation.
3.2.3 **EFFECT OF STRESS ON DIFFUSION**

Application of a stress made a significant difference to the width of the diffusion zone in this system. Photomicrographs of the diffusion zone at different stresses are shown in fig. 14. Fig. 15 shows the thickness of the Ag$_3$Sb as a function of stress at 350°C and 400°C. It was observed that at 350°C the thickness of the diffusion zone increased with increasing stress—from 250Å at 0 psi to 400Å at 800 psi, whilst beyond 800 psi no variation in the width of the diffusion zone was noticed. This would mean that there is an apparent increase in the diffusion coefficient by 150 pct when the stress is increased from zero to 800 psi. Similar behaviour was observed at 400°C, the rate of increase of the width of the diffusion zone with stress being higher than that at the lower temperature, indicating that the stress effect is not characteristic of just one temperature. It was also observed that the limiting stress beyond which the diffusion width was constant seemed to be higher at higher temperatures.

3.2.4 **KINETICS**

Curves showing the growth of Ag$_3$Sb at various stresses are shown in fig. 16. In every case growth was parabolic indicating a mechanism controlled by diffusion. The kinetic curves all pass through the origin indicating that delayed nucleation of the Ag$_3$Sb phase was not responsible for the stress effect and that it was a real growth effect. The growth rate $\alpha$ in cm/$\sqrt{\text{sec}}$ is plotted as a function of stress in fig. 17 and it can be seen that it increases by a factor of 1.6 on going from zero to 800 psi.

A series of tests were carried out in which diffusion was
Fig. 14 Photomicrographs of the diffusion zone in Ag-Sb annealed at 350°C for 25 hrs. at various pressures. 50 x.
Graph of the thickness of Ag₃Sb as a function of stress following diffusion for 25 hrs. at 350°C and 400°C
Fig. 16  Growth of Ag$_3$Sb at 350°C at 50, 300 and 1000 psi
Fig. 17 Growth rate of Ag₃Sb at 350°C as a function of stress
allowed to take place at low pressure following an initial high pressure diffusion anneal. Specimens were initially diffused at 350°C for 4 hours under a stress of 1000 psi to give a wide band of Ag₃Sb after which the stress was released and diffusion was allowed to take place at zero stress for various times. The results are plotted in fig. 18 and 19. It can be seen in fig. 18 that the width of the diffusion zone increased with increasing time, following the same curve as the test at 1000 psi for about 20 hours, after which the growth rate decreased and the curve began to approach the zero psi curve. Fig. 19 shows that parabolic growth is obeyed in two different regions. After the stress was released, the Ag₃Sb phase continued to grow at the rate characteristic of a 1000 psi stress. After a long time of anneal, however, the growth rate decreased to the 0-psi value. Hence when stress is altered in the diffusing system there is a transient effect before the growth rate characteristic of the new stress is established.

3.2.5 HYDROSTATIC TEST

Hydrostatic tests were carried out to see whether there was any difference in growth rate between uniaxial compressive stress and triaxial hydrostatic pressure. Specimens were prebonded at 350°C for 1 hour under a compressive stress of 1000 psi and then diffused under a hydrostatic pressure of 400 psi at 350°C for different times. The results are plotted in fig. 20. It can be seen that the growth rate under hydrostatic pressure is much less than the growth rate under a compressive load of the same magnitude. Indeed, the growth rate under hydrostatic pressure very closely resembles that for a compressive test at 0 psi. Hence application of a hydrostatic pressure to the Ag-Sb system
Fig. 18 Growth of Ag$_3$Sb at 350°C. Growth took place initially at 1000 psi for 4 hrs. after which stress was released and diffusion allowed at zero stress. Growth tests at 1000 psi and zero psi are included for comparison.
Fig. 19 Parabolic plot of the results shown in fig. 18
Fig. 20  Growth of Ag₃Sb at 350°C under a hydrostatic pressure of 400 psi. Specimens prebonded for 1 hr. at 1000 psi. Normal growth tests at zero psi and 400 psi are included for comparison purposes.
did not produce any effect on the growth rate and only a compressive load is of any significance.

3.2.6 KIRKENDALL EXPERIMENTS

Kirkendall tests were carried out using 0.001" dia. tungsten wire markers. The results are shown in fig. 21. It was observed that the markers stayed at the Ag/Ag₃Sb interface indicating that silver is the diffusing species. Fig. 21 (a) - (d) show Kirkendall marker experiments carried out at 350°C under 1000 psi for different lengths of time. It can be seen that the markers initially act as barriers to diffusion and that the diffusion zone has zero width at the marker positions. As diffusion proceeds lateral diffusion takes place to give a band of Ag₃Sb at the marker locations (fig. 21 (c)), and with increasing time (fig. 21 (d)) the thickness of the diffusion zone at these positions becomes comparable with the width of the diffusion zone away from the markers. Ledges of silver and antimony formed at the markers in the initial stages of diffusion gradually decay until both the Ag/Ag₃Sb and the Ag₃Sb/Sb boundaries become fairly planar. However, small sharp wedges at the Ag₃Sb/Sb interface are retained for a long time. Fig. 22 shows that the height of the silver and antimony ledges depends on the size of the markers, and so on the amount of lateral diffusion required.

In order to obtain a qualitative idea of the Kirkendall effect in a system not sensitive to stress, experiments were carried out on a Cu/α-Brass couple using different size markers. Fig. 23 shows a micrograph of the diffusion zone. Observing the structural changes in the diffusion zone, and taking them to correspond to composition contours, it
Fig. 21 Photomicrographs of Kirkendall marker experiments in Ag-Sb, for specimens annealed for different times at 350°C under 1000 psi. 22 x
Fig. 22 Photomicrographs of the Kirkendall experiment in Ag-Sb with different marker wire diameters. Specimen annealed for 50 hr. at 350°C under 1000 psi stress. 30 x
Fig. 23 Photomicrograph of Kirkendall experiment in Cu/α-Brass with different size markers. Experiment carried out at 900°C for 60 hrs. 23 x
can be seen that there is no ledge formation, except adjacent to the largest marker. This would suggest that formation of ledges at the Kirkendall marker positions is characteristic of a stress sensitive system.

3.2.7 DISCUSSION

The stress effect in diffusion in Ag-Sb is a true growth effect and does not depend on pressure influenced nucleation. As discussed in the Introduction there are three possible effects which can account for a pressure influenced growth - variation of the diffusion coefficient, variation of the phase boundary composition and modification of the Kirkendall porosity. A very large Kirkendall shift is observed in this system indicating silver to be the diffusing species and so there would be a large vacancy flux towards the silver, these vacancies condensing mainly at the Ag/Ag$_3$Sb interface. Hence conditions are ideal for the development of the Kirkendall porosity.

The growth rate reached a maximum at 800 psi and then became constant, independent of applied pressure. This would be very difficult to explain from the viewpoint of changes in the diffusion coefficient and phase boundary composition since these would be expected to increase continuously with applied stress. However, once the stress applied is sufficiently great to give an unrestricted flux across the Ag/Ag$_3$Sb interface with no restriction from the incipient Kirkendall porosity, pressure would have no effect on the growth rate.

Application of a hydrostatic pressure did not have any effect on the growth rate, unlike compressive stress. This would again be impossible to explain from changes in the phase boundary composition and diffusion
coefficient since hydrostatic pressure should be just as efficient in altering the diffusion coefficient and phase boundary compositions as compressive stress. The results can be explained, however, from the viewpoint of the Kirkendall porosity. Because of the defective nature of the Ag/Ag$_3$Sb interface resulting from the Kirkendall porosity the outside hydrostatic pressure may introduce a pressure at the boundary, which may be equivalent to the external pressure and this will eliminate the effective pressure across the interface. Hence, although compressive stresses are developed across certain portions of the diffusion zone there is no compressive force at the critical Ag/Ag$_3$Sb boundary and so no improvement in the bonding. With compressive loading, however, the situation is completely different since the full load is developed across the complete diffusion zone including the Ag/Ag$_3$Sb interface. The bonding at this interface is, therefore, improved and the flux of atoms increased.

Experiments in which pressure was suddenly reduced in the course of a diffusion anneal show that once a good bond is developed at an interface it tends to be retained for a short period before development of a poorer bond characteristic of lower pressure. This is reasonable, since as discussed in the Introduction (p. 11) the tendency for development of the Kirkendall porosity is greatest at the beginning of diffusion. If a good bond is established at this time, it will tend to be maintained for a short time after the pressure is removed before the growth rate characteristic of the lower pressure is developed.

The development of ledges at the Kirkendall markers is much more evident in Ag-Sb than in Cu-α brass and is considered to be due to the stress sensitivity in Ag-Sb. The maximum height of ledges increases with
increasing marker size and reflects the amount of lateral diffusion required with increasing wire diameter. Ledges at the silver interface last much longer than those at the antimony interface and are caused by restricted flux of silver atoms into the $\text{Ag}_3\text{Sb}$ at the interface normal to the direction of diffusion. The reason for this is that there is no applied compressive stress in this direction and so flux of silver atoms will be quite restricted in comparison with the normal diffusion direction. These results are again in agreement with the mechanism of restricted flux due to the incipient Kirkendall porosity.

3.3 **SILVER-SELENIUM SYSTEM**

The results in the Ag-Se system were very similar to those in Ag-Sb and for this reason a less detailed investigation was carried out.

3.3.1 **THE PHASE DIAGRAM**

The phase diagram of the Ag-Se system is shown in fig. 24. Only one intermetallic phase, $\text{Ag}_2\text{Se}$ (26.8 wt pct Se), is stable. This phase undergoes an order-disorder transformation at $128^\circ\text{C}$ similar to that in $\text{Ag}_2\text{S}$. The high temperature $\beta$-modification has a $\text{CaF}_2$ type structure (cubic) with $a = 4.993\text{Å}$, and the low temperature $\alpha$-phase is either orthorhombic, monoclinic or tetragonal. The large Se ions lie in fixed lattice positions and the smaller Ag ions diffuse through interstitial sites between the Se ions. At low temperatures the Ag ions are distributed at random among the interstitial sites and have a very high mobility. Specific volume calculations indicate that there is a 3.2 pct expansion.
Fig. 24  Phase diagram of Ag-Se (Hansen)
in forming Ag₂Se from silver and selenium.

3.3.2 IDENTIFICATION OF THE PHASE

Diffusion experiments were carried out at 130°C just above the polymorphic transition temperature of Ag₂Se. As expected only one phase appeared in the diffusion zone and the electron probe traverse confirmed that the composition corresponded to Ag₂Se (fig. 25). The X-ray diffraction analysis (Appendix 1) indicated that the phase was the high temperature β - phase as expected from the temperature of the experiment.

3.3.3 EFFECT OF STRESS ON DIFFUSION

The width of Ag₂Se in the diffusion zone showed a significant sensitivity to stress. Fig. 25 shows the variation of the thickness of the diffusion zone with stress following diffusion for 25 hours at 130°C. It was observed that the width of Ag₂Se increased with increasing stress from 137μ at zero stress to 392μ at 800 psi, beyond which there was no effect. Hence the effect observed in this system is similar to that in Ag-Sb, except that the increase in width is somewhat greater.

3.3.4 KINETICS

Curves showing the growth of Ag₂Se at various stresses are shown in fig. 27. In every case the growth was parabolic, indicating a mechanism controlled by a diffusion process.

3.3.5 KIRKENDALL TEST

A photomicrograph of a typical marker experiment is shown in fig. 28. The markers were at the Ag/Ag₂Se interface indicating that silver is
Fig. 25  Electron microprobe traverse for a Ag-Se diffusion couple annealed at 130°C for 25 hrs. at 200 psi. Composition measured using Se-Kα radiation
Fig. 26  Thickness of Ag$_2$Se as a function of stress following diffusion for 25 hrs. at 130°C
Fig. 27  Growth of Ag$_2$Se at 130°C at different stresses
Fig. 28  Micrograph showing Kirkendall markers. Couple diffused for 25 hrs. at 130°C and 400 psi. 30 x
the diffusing species as expected from the structure of Ag\textsubscript{2}Se (see p. 60). The figure also shows ledges of silver at the Ag/Ag\textsubscript{2}Se boundary similar to those in Ag-Sb. These can be explained by differences in the flux across the Ag\textsubscript{2}Se/Ag interface perpendicular and parallel to the applied stress.

### 3.3.6 DISCUSSION

It was unfortunate that the temperature used in studying diffusion in this system was 130°C, just at the transformation temperature of 128 ± 5°C. However, in view of the consistency of the data it would appear that all measurements were carried out above the transition temperature and the proximity of the transformation temperature did not significantly affect the results.

The effect of stress in the Ag-Se system is very similar to that observed in Ag-Sb except that the variation is rather greater. The growth rate reaches a maximum at 800 psi and then remains constant independent of stress just as in Ag-Sb. The explanation for stress sensitivity in Ag-Se must be the same as in Ag-Sb in view of the similarity of the results. Applying a stress to the Ag\textsubscript{2}Se/Ag interface increases the Ag flux across the boundary by improving the interface. At 800 psi, the Ag flux is unrestricted and no further stress effect is observed.

Specific volume calculations show a 3.2 pct increase in forming Ag\textsubscript{2}Se and a 6.1 pct decrease in forming Ag\textsubscript{3}Sb. Since both systems show very similar effects of stress it can be concluded that this has no effect on the stress sensitivity.
3.4 **NICHEL-ANTIMONY SYSTEM**

Diffusion couples of Ni-Sb showed that there were three intermetallic compounds in the diffusion zone, rather than just the one phase observed in Ag-Sb and Ag-Se. Hence the results will be considered in a little more detail than in Ag-Se.

### 3.4.1 THE PHASE DIAGRAM

The most recent phase diagram for the Ni-Sb system is shown in fig. 29. The low temperature portion of the diagram is uncertain, especially in the composition range of 24 - 31 at. pct Sb. Hansen suggests that five intermetallics are stable at 400°C, the temperature of the experiments. These phases are listed in Table 3, together with the reported crystal structures and specific volumes. The β-phase ($\text{Ni}_3\text{Sb}_2$) is reported to undergo a martensitic reaction ($\beta'$) below 580°C. However, alloys of 33.3 at. pct Sb, annealed above and below the transformation temperature and quenched have the same structure, thus throwing some doubt on the $\beta \rightarrow \beta'$ transformation. The structure of Ni-Sb is uncertain and different researchers have taken it to be either hexagonal, cubic, or orthorhombic.

### 3.4.2 IDENTIFICATION OF THE PHASES

Three out of the five stable phases were observed in the diffusion zone after a 400°C diffusion anneal. Attempts were made to identify these phases by electron probe analysis and by X-ray diffraction. The Ni-rich and Sb-rich phases in the diffusion zone were very narrow (10 - 20µ) and X-ray diffractometric analysis of these phases was not possible. d-spacing values and X-ray intensities obtained for the phase in the middle
Fig. 29  The phase diagram of Ni-Sb \( (\text{Hansen}^7) \)
**TABLE 3**

CHARACTERISTICS OF INTERMEDIATE PHASES IN Ni-Sb AT 400°C

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition at 400°C wt pct Sb</th>
<th>Crystal Structure</th>
<th>Specific Volume c.c./gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{15}$Sb</td>
<td>12.4</td>
<td>Superstructure of cubic lattice with 32 atoms/cell</td>
<td>0.1072$^{76}$</td>
</tr>
<tr>
<td>Ni$_3$Sb</td>
<td>38.3</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Ni$_5$Sb$_2$</td>
<td>41.1 - 44.2</td>
<td>Tetragonal with 2 atoms/cell</td>
<td>0.1238$^{73}$</td>
</tr>
<tr>
<td>NiSb</td>
<td>65.5 - 70.0</td>
<td>Hexagonal with 52 atoms/cell</td>
<td>0.1325$^{77}$</td>
</tr>
<tr>
<td>NiSb$_2$</td>
<td>83.2</td>
<td>Orthorhombic$^{73}$</td>
<td>0.1274$^{78}$</td>
</tr>
</tbody>
</table>
are shown in Table 4. There was no agreement with any of the suggested crystal structures for Ni₃Sb and NiSb. However, as may be seen in Table 4, there was good agreement between the intense lines in the diffractometer trace and the high temperature structure of Ni₃Sb₂. The extra low intensity lines in the diffractometer trace may conceivably be related to a superlattice structure characteristic of the low temperature.

An electron probe traverse for the diffusion couple is shown in fig. 29. The phases adjacent to nickel and antimony were less than 20μ thick and quantitative analysis was not possible with the existing U.B.C. electron probe which had a spot diameter of ~ 10μ. The probe trace shown in fig. 30 was carried out on a J.E.O.L. Co. JXA-3A electron probe with an electron beam diameter of less than 1μ.* The phase in the middle of the diffusion zone gives a composition of 43.1 wt pct Sb and corresponds to the composition of Ni₅Sb₂ in agreement with X-ray analysis. The Ni-rich phase has a composition of 36.8 wt pct Sb, which is less than, but fairly close to, the composition of Ni₃Sb (40.0 wt pct Sb). The composition of the phase on the antimony side of the diffusion couple, as given by the probe analysis (60 wt pct Sb), does not agree well with any of the compounds given in the phase diagram. This is probably due to the phase being too thin for accurate analysis. The phase closest in composition to it is NiSb and occurs at 66.0 - 70 wt pct Sb. Thus the phases in the diffusion zone are, most probably, NiSb, Ni₅Sb₂ and Ni₃Sb.

* The author would like to express his appreciation to Mr. J. Roussos of J.E.O.L. Co Ltd. for his help in carrying out this analysis.
<table>
<thead>
<tr>
<th>( d )</th>
<th>( \text{I/I}_0 )</th>
<th>( \text{ASTM Standard card for } \beta\text{-Ni}_5\text{Sb}_2 )</th>
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<td>1.36</td>
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</tbody>
</table>
Fig. 30  Electron probe traverse for Ni-Sb diffusion couple aged for 49 hrs. at 400°C at 400 psi. Profile measured using Sb-L radiation
3.4.3 **THE EFFECT OF STRESS ON DIFFUSION**

Application of stress was found to have a large effect on the width of the diffusion zone. Fig. 31 shows photomicrographs of the diffusion zones obtained by annealing specimens at different stresses for 25 hours at 400°C. Fig. 32 shows the width of the diffusion zone as a function of stress. The maximum stress was limited to 1500 psi since above this antimony began to creep. Fig. 31 shows that Ni₃Sb and NiSb exhibit a very small increase in thickness with increasing stress. The Ni₅Sb₂ phase is however very sensitive to applied stress with its thickness increasing linearly with stress - from 26.0μ at zero stress to 68.0μ at 1500 psi. The stress characteristics in this system are different from those in Ag-Sb and Ag-Se, since in this system there is no apparent tendency for the thickness of the phase to reach a limiting value with increasing stress.

3.4.4 **KINETICS**

Typical growth curves are shown in fig. 33 and fig. 34. The growth of all three phases at all pressures is parabolic with time, indicating a mechanism controlled by diffusion. All the curves pass through the origin suggesting that there is no delayed nucleation and that the effect of the stress is a genuine growth effect. Fig. 35 shows the growth rate (α) of Ni₅Sb₂ as a function of stress. The growth rate increases apparently linearly with stress - from 0.88 x 10⁻⁵ cm/√sec. at zero stress to 2.2 x 10⁻⁵ cm/√sec. at 1500 psi.

A series of tests were carried out in which diffusion took place at a low stress following a high pressure anneal. Specimens were initially
Fig. 31 Photomicrographs of the diffusion zone in Ni-Sb annealed at 400°C for 25 hrs. at different stresses. 600 x
Fig. 32  Thickness of the intermediate phases in diffusion couples of Ni-Sb, annealed at 400°C for 25 hrs, as a function of stress.
Fig. 33 Growth of the intermetallic phases in Ni-Sb at 400°C and 200 psi
Fig. 34  Growth of the intermetallic phases in Ni-Sb at 400°C and 500 psi
Growth rate in cm/√sec x 10^5

Fig. 35

Growth rate of Ni₅Sb₂ at 400°C as a function of stress

Stress in psi

200 400 600 800 1000 1200 1400 1600
diffused at 400°C for 4 hours under a stress of 1000 psi to give a wide band of Ni₅Sb₂, after which the stress was released and diffusion experiments were carried out for various lengths of time at zero stress. The results are shown in fig. 36 and fig. 37. It can be seen from fig. 36 that the width of Ni₅Sb₂ increases with increasing time, approaching the curvature of the 0-psi curve after long diffusion times. Fig. 37 shows that a parabolic growth law is obeyed at longer times of diffusion, the growth rate being the same as that at zero psi. There is a short transient period before the growth rate characteristic of zero stress is established. The growth rates of Ni₃Sb and NiSb follow the same rate as that of the 1000 psi experiment. Growth of these phases is not significantly affected by stress, hence no effect should be expected on removal of the stress.

3.4.5 KIRKENDALL TESTS

A typical micrograph of a Kirkendall marker experiment is shown in fig. 38. The markers lie on the Ni/Ni₅Sb₂ boundary suggesting that nickel is the diffusing species in the Ni₅Sb₂ phase. Ledges of nickel are observed at the marker position as in Ag-Sb and Ag-Se.

3.4.6 DISCUSSION

An applied compressive stress has a large effect on diffusion in Ni-Sb with the thickness of the Ni₅Sb₂ phase increasing by a factor of 2.6 from zero psi to 1500 psi. Unlike Ag-Sb and Ag-Se, the thickness of the Ni₅Sb₂ phase does not appear to approach a limiting value with increasing stress. In this regard the results are similar to those observed in Cu-Te⁶ and Al-U³ (see page 4,6).
Fig. 36  Growth of Ni$_2$Sb, when an initial stress of 1000 psi is released after 4 hrs. of anneal at 400°C. Normal growth curves at zero psi and 1000 psi are included for comparison.
Fig. 37 Parabolic plots of the results of the same experiment as in Fig. 36
Fig. 38 Micrograph of Kirkendall experiment. Specimen aged at 400°C at 1000 psi for 237 hrs.
In view of the large stress sensitivity in Ni-Sb, it seems most reasonable that in this system, just as in Ag-Sb and Ag-Se, the effect of stress is to limit the amount of the Kirkendall porosity. This explanation has also been used in the Al-U and Cu-Te systems. The Kirkendall marker experiment suggests that nickel is the diffusing species in Ni$_5$Sb$_2$ and NiSb. In Ni$_3$Sb, however, the situation is rather indefinite since the markers lie at the Ni/Ni$_5$Sb$_2$ boundary and it is not possible to say whether nickel or antimony is the diffusing species. Growth of Ni$_3$Sb, which is the phase adjacent to the nickel, is not significantly affected by the applied stress and the main effect of stress is seen in the adjacent Ni$_5$Sb$_2$ phase. These observations are somewhat different from Al-U and Cu-Te, where the stress sensitive phase is adjacent to the metal with the larger diffusion coefficient. Thus, it seems that in Ni-Sb the critical interface is between Ni$_3$Sb and Ni$_5$Sb$_2$. Two suggestions may be made to account for this. The first is that diffusion in Ni$_3$Sb is due to the motion of antimony atoms. The Kirkendall marker experiments are not in disagreement with this. Hence there is a vacancy flux through Ni$_5$Sb$_2$ to the Ni$_5$Sb$_2$/Ni$_3$Sb interface caused by the flux of nickel atoms and there is also a vacancy flux from Ni$_3$Sb to the same interface caused by the flux of antimony atoms. Both vacancy fluxes condense at the same interface, thus weakening the Ni$_5$Sb$_2$/Ni$_3$Sb interface. The other possible explanation is that the Ni/Ni$_3$Sb boundary may be better than the Ni$_3$Sb/Ni$_5$Sb$_2$ interface. Nickel atoms will be considered to diffuse in both Ni$_3$Sb and Ni$_5$Sb$_2$. Growth of Ni$_3$Sb is very slow in comparison with Ni$_5$Sb$_2$. Hence the vacancy flux condensing at the Ni$_5$Sb$_2$/Ni$_3$Sb interface is almost as great as that at the Ni/Ni$_3$Sb interface. The interface between Ni$_3$Sb and Ni$_5$Sb$_2$ is defective, however, and so the incipient Kirkendall porosity will develop at this interface rather
than at the Ni/Ni₃Sb boundary.

Whichever of these two suggestions is correct, there is no doubt that the stress effect arises because of the atom transfer across the Ni₃Sb/Ni₅Sb₂ interface. Application of a compressive load improves this bond and so increases the atom transfer into Ni₅Sb₂, thus causing the growth rate of this phase to increase. If the first mechanism is operative, improvement of the Ni₃Sb/Ni₅Sb₂ boundary would increase the antimony flux into the Ni₃Sb phase with increasing stress. However, the diffusion coefficient in this phase is very small as seen from its small growth rates, even at high stresses, and hence the change in flux would not make a significant change in the growth rate. The nickel flux across the Ni₅Sb₂/Ni₂Sb interface is quite small and so there is only a slight tendency for the transfer of atoms across this interface to be restricted. Hence NiSb would be expected to grow essentially independent of applied stress, and this is observed experimentally.

The Kirkendall experiment (fig. 36 (b)) provides proof that transfer of nickel atoms into Ni₃Sb is easier than into Ni₅Sb₂ at low stresses. This can be seen by examining the nickel ledge under the tungsten marker, which is thinner when surrounded by Ni₃Sb than by Ni₅Sb₂. This is shown in the schematic representation in fig. 39.

![Schematic representation of diffusion around markers in Ni-Sb](image)

**Fig. 39** Schematic representation of diffusion around markers in Ni-Sb
There is no compressive stress across the Ni/\text{Ni}_3\text{Sb}_2 or Ni/\text{Ni}_5\text{Sb}_2 interfaces in the lateral direction, while the full applied stress is developed across the \text{Ni}_3\text{Sb}/\text{Ni}_5\text{Sb}_2 interface. Hence there is no restriction to atom transfer across the \text{Ni}_3\text{Sb}/\text{Ni}_5\text{Sb}_2 boundary. \text{Ni}_3\text{Sb} grows in the lateral direction into the nickel ledge whereas growth of \text{Ni}_5\text{Sb}_2 in this direction is restricted and hence the relative width of the nickel ledge in the two regions is a true measure of the ease of transfer of atoms into \text{Ni}_3\text{Sb} and \text{Ni}_5\text{Sb}_2.

The growth rate of \text{Ni}_5\text{Sb}_2 appears to increase continuously with the applied stress up to 1500 psi. It might be thought that this dependence over such a wide range of stress was characteristic of a diffusion couple with more than one intermetallic compound, since systems like Cu-Te and Al-U which also have 2-3 phases in the diffusion zone show a similar stress effect. It is, however, very difficult to suggest any explanation as to why the effect of stress in a system with one intermetallic phase should be different from that in a system with 2-3 intermetallic compounds, since an equivalent vacancy flux should be condensing in both cases. It seems more likely that in systems like Ni-Sb, Cu-Te and U-Al, one of the phases has a very high growth rate but because of the corresponding very large vacancy flux a high pressure is necessary to establish a good interface. The maximum stress of 1500 psi used in the experiments with Ni-Sb couples was presumably not sufficient for a good interface to develop.

Experiments in which the stress was suddenly released in the course of a diffusion anneal showed a short transient period before the growth rate characteristic of the new stress was attained. This observation is similar to that in Ag-Sb, and indicates that a bond across the interface
characteristic of a high applied stress will be retained for a short time after the stress is removed until the bond characteristic of the new stress develops.

The Ni-Sb system showed a wide variation in the growth rates of the various stable phases. Two of the five stable phases did not appear in the diffusion zone at all, two other phases have very narrow widths, whilst the fifth phase ($\text{Ni}_5\text{Sb}_2$) is very much thicker than any other, even though its growth is restricted by transfer of atoms across its interface. This suggests that the diffusion coefficient in $\text{Ni}_5\text{Sb}_2$ is much higher than in any other phase in this alloy system. This is related, presumably, to a defect structure in this phase. However, because of uncertainties in the crystal structure this fast growth rate cannot be discussed in a quantitative manner.
3.5 COPPER-SELENIUM SYSTEM

Diffusion couples of Cu-Se annealed at 170°C showed two phases in the diffusion zone. The stress effect in this system was different from that observed in Ni-Sb and the results will, therefore, be presented in some detail.

3.5.1 THE PHASE DIAGRAM

The complete phase diagram of the Cu-Se system is not available in the literature. Hansen reports the existence of three intermetallic phases, Cu₂Se, Cu₃Se₂ and CuSe, with highly restricted composition ranges. Cu₂Se (38.22 wt pct Se) is f.c.c. with 12 atoms per unit cell. This compound is highly defective and should be written Cu₂₋ₓSe with a maximum value of x = 0.14. At the Se-rich end of the composition range of Cu₂₋ₓSe, the f.c.c. structure is retained to room temperature, while, at the Cu-rich end, a series of low temperature phase transformations occur and it has been reported that no less than seven different crystal structures exist. Cu₃Se₂ (45.4 wt pct Se) is orthorhombic with 20 atoms per unit cell. This compound is also very defective with the excess cations occupying interstitial positions. CuSe (55.4 wt pct Se) is hexagonal, most likely isotypic with the CuS structure.

3.5.2 IDENTIFICATION OF THE PHASES

Only two phases were observed in the diffusion zone. They were identified by electron microprobe analysis and by X-ray diffraction technique. The probe traverse is shown in fig. 40. Compositions of 36.2 wt pct Se found for the Cu-rich phase and 46.5 wt pct Se for the Se-rich phase agreed well with the composition of Cu₂Se (38.2 pct Se) and Cu₃Se₂ (45.4 wt pct Se),
Fig. 40  Electron probe traverse of the diffusion zone in a Cu-Se couple annealed at 170°C for 25 hrs. at 200 psi
respectively. The probe traverse did not show any solid solubility of the elements in one another nor any concentration gradient within the phases. X-ray diffraction confirmed that the Se-rich phase was Cu$_3$Se$_2$ (Appendix 1). The d-spacings obtained for the Cu-rich phase did not correspond to those of the high temperature form of Cu$_2$Se. However, as discussed in page 88 there are several complex low temperature transitions in this phase and the observed structure may well be one of these.

3.4.3 THE EFFECT OF STRESS ON DIFFUSION

Application of stress has a large effect on the width of the diffusion zone in this system, significantly greater than in any of the other systems investigated in this work. Fig. 41 shows the thickness of the diffusion zone obtained by annealing specimens for 25 hours at 170°C, as a function of stress. It was seen that the width of Cu$_2$Se increased linearly with increasing stress - from 30µ at zero stress to 660µ at 1500 psi. The thickness of Cu$_2$Se comprised 76.0 pct of the total diffusion zone width at 1500 psi compared to 9.0 pct at zero stress. The only other system in which this magnitude of stress sensitivity has been observed is Cu-Te. The width of Cu$_3$Se$_2$ decreased with increasing stress - from 310µ at zero stress to 215µ at 1500 psi. The effect on Cu$_3$Se$_2$, however, was small compared to that in Cu$_2$Se.

3.4.4 KINETICS

Typical growth curves at 50, 400 and 1000 psi are shown in fig. 42 and 43 and others are given in Appendix 2. At high pressures (1000 psi) growth of both phases was parabolic indicating diffusion was rate determining. At low stresses (50 and 400 psi) there was an incubation period before Cu$_2$Se
Fig. 41  Thickness of Cu$_2$Se and Cu$_3$Se obtained by 25 hr. anneal at 170$^\circ$C as a function of stress
Fig. 42  Growth of Cu₂Se at 170°C and 50, 400 and 1000 psi
Fig. 43  Growth of Cu$_3$Se$_2$ at 170°C and 50, 400 and 1000 psi.
forms and during which growth of Cu$_3$Se$_2$ was very slow. This incubation
time decreased linearly with increasing stress as shown in fig. 44 and
above 560 psi no incubation period was observed. In considering
x vs $\sqrt{t}$ plots it seemed most reasonable that the time origin for the
Cu$_2$Se phase be taken as the time necessary for its nucleation. Before the
Cu$_3$Se$_2$ phase started to grow quickly it achieved a certain thickness and
the time origin for this phase could be found by extrapolating the true
growth curve of Cu$_3$Se$_2$ to zero thickness. As seen in fig. 45, this
method gives plots which are parabolic, indicating that the procedures for
determining the time origin are reasonable and that the growth is diffusion
controlled at low stresses. Even when the time origin is taken as the
beginning of diffusion, the x vs $\sqrt{t}$ plots give straight lines, but such plots
do not have theoretical validity and hence are not used for analysis of the
results. Fig. 46 shows the parabolic growth at 1000 psi where there is
no incubation period. Growth rates of Cu$_2$Se and Cu$_3$Se are plotted as a
function of stress in fig. 47. It was observed that the growth rate of
Cu$_2$Se increased apparently linearly with the stress, and that the growth
rate of Cu$_3$Se$_2$ decreased apparently linearly with the stress.

A series of tests were carried out in which diffusion was
allowed to take place at low pressure following an initial high stress
diffusion anneal. Specimens were annealed at 170°C for 4 hours under a
stress of 1000 psi to give a wide band of Cu$_2$Se after which the pressure
was released and diffusion was allowed to proceed at zero psi. The
results are given in fig. 48. It was seen that the thickness of Cu$_2$Se
decreased continuously with increasing diffusion time and after 45 hours it
had disappeared completely. The Cu$_3$Se$_2$ grew at the expense of the Cu$_2$Se,
Fig. 44 Incubation period for Cu₂Se at 170°C as a function of applied stress
Fig. 45 Parabolic growth plots for Cu$_2$Se and Cu$_3$Se$_2$ at 170°C at 50 psi. Time scale corrected for the incubation period for Cu$_2$Se and the start of fast growth for Cu$_3$Se$_2$. 
Fig. 46  Growth of Cu$_2$Se and Cu$_3$Se$_2$ at 170°C at 1000 psi
Fig. 47  Growth rates of Cu$_2$Se and Cu$_3$Se$_2$ at 170°C as a function of stress
Fig. 48  Graph illustrating the shrinking of Cu$_2$Se at 170°C when an initial stress of 1000 psi is released after 4 hr. anneal and diffusion allowed at zero stress.
although its growth rate was very much less than would be expected from normal growth measurements at zero stress. It should be noted that there was still some growth of Cu$_3$Se$_2$ even after the Cu$_2$Se had disappeared, indicating that some transfer of atoms into the diffusion zone was taking place.

The above results are significantly different from similar tests in the other systems investigated. For example, other systems have shown the development of growth rates characteristic of the new stress applied. In Cu-Se, the growth of Cu$_3$Se$_2$ is much slower than is characteristic of the zero stress whilst Cu$_2$Se would be expected to shrink but not disappear completely. For this reason a second set of experiments was carried out in which diffusion was allowed to take place initially for 4 hours at 1000 psi and then the pressure was reduced to 120 psi rather than to the zero psi. The results in fig. 49 show that the Cu$_2$Se phase still disappeared although at 120 psi it should have a fairly high growth rate. However, the Cu$_3$Se$_2$ now grew at a rate which was close to the expected 120 psi growth rate.

3.4.5 HYDROSTATIC TEST

Hydrostatic tests were carried out in order to study the difference between the effect of uniaxial stress and hydrostatic pressure in this rather complicated system. Specimens were prebonded at 170°C for one hour under a compressive stress of 1000 psi and then diffusion continued under a hydrostatic pressure of 400 psi at 170°C for different lengths of time. The results are shown in fig. 50. It was observed that the Cu$_2$Se continued to grow for about 6 hours after which the width of this phase began
Fig. 49 Graph showing the shrinking of Cu₂Se at 170°C when initial stress of 1000 psi is released after 4 hrs. and diffusion allowed under a new stress of 120 psi.
Fig. 50  Graph showing the growth of Cu$_2$Se and Cu$_3$Se$_2$ under a hydrostatic pressure of 400 psi at 170°C
to decrease and it disappeared after about 100 hours. The Cu$_3$Se$_2$ phase initially continued to grow at the rate characteristic of 1000 psi stress. However, after the Cu$_2$Se started regressing the growth rate of Cu$_3$Se$_2$ increased by a factor of 2.2. The disappearance of Cu$_2$Se at a hydrostatic pressure of 400 psi is very similar to the disappearance of Cu$_2$Se under a compressive stress of zero and 120 psi following an initial high pressure anneal (fig. 48 and 49). This suggests that in this system hydrostatic pressure has no significant effect on growth rates and only compressive loading is of any importance. Similar results were also found in the Ag-Sb system.

3.4.6 KIRKENDALL TEST

A photomicrograph of the diffusion zone in a Kirkendall marker experiment is shown in fig. 51. It can be seen that the tungsten markers stayed at the Cu/Cu$_2$Se interface suggesting that copper was the diffusing species. Ledges of copper were observed at the marker position as in the systems reported previously.

3.4.7 DISCUSSION

It has been shown that diffusion in Cu-Se is very sensitive to compressive stresses with the width of Cu$_2$Se at 1500 psi being 22 times that at zero stress. There seems little doubt that this stress effect in Cu-Se is due to the elimination of porosity at the Cu/Cu$_2$Se interface by the applied pressure, just as in the other systems investigated in this study.
Fig. 51 Photomicrograph of Kirkendall experiment in Cu-Se at 170°C for 25 hrs. under 1000 psi. 22 x
At low stresses the $\text{Cu}_3\text{Se}_2$ phase grows much faster than $\text{Cu}_2\text{Se}$. This would be expected since with a small copper flux into the diffusion zone there would be a tendency for the formation of the Se-rich phase. With increasing stress the copper flux increases and growth of the Cu-rich $\text{Cu}_2\text{Se}$ phase is facilitated and its thickness increases linearly with the applied stress. The stress dependence in this phase is thus similar to that in Ni-Sb and as discussed in page 86 is characteristic of a phase with a high intrinsic diffusion coefficient.

The thickness of $\text{Cu}_3\text{Se}_2$ decreases with increasing stress. Growth of this phase depends on the flux of copper atoms from $\text{Cu}_2\text{Se}$ into $\text{Cu}_3\text{Se}_2$. This flux depends primarily on the concentration gradient in the $\text{Cu}_2\text{Se}$ and as can be seen in fig. 52, this is greatest when $\text{Cu}_2\text{Se}$ is thin i.e. at low stresses. Similar reductions in thickness with increasing pressure occur in the $\text{Cu}_4\text{Te}_3$ and CuTe phases in Cu-Te.
Cu-Se is different from other systems examined so far in that there is a nucleation period before the Cu$_2$Se forms and during which growth of Cu$_3$Se$_2$ is slow. This nucleation time appears to decrease linearly with pressure and varies from 6.2 hr. at zero stress to zero time above 560 psi. This nucleation time appears to be indicative of poor bonding across the interface of the diffusion couple.

Tests in which the pressure was suddenly reduced in the course of a diffusion anneal also gave results in Cu-Se which were different from the systems discussed before. In other systems, the growth rate which developed on removal of the applied stress was characteristic of the new pressure. In Cu-Se at zero stress, the growth rate was significantly less for both the Cu$_2$Se and Cu$_3$Se$_2$ phases. Some copper atoms entered the diffusion zone from the pure metal since the Cu$_3$Se$_2$ phase continued to grow after the Cu$_2$Se phase had disappeared. However, this growth rate was very small indicating that the Cu/Cu$_3$Se$_2$ interface was very defective. At 120 psi, Cu$_3$Se$_2$ grew at the rate characteristic of the applied pressure. However, the Cu$_2$Se phase still did not grow, suggesting that transfer of atoms from copper into the diffusion zone is still restricted.

The incubation period at the beginning of diffusion and the slow diffusion which occurs on removal of the stress after an initial high pressure anneal, indicate a tendency to form poor interfaces in this system.

As will be shown in the next section similar results were obtained in the Cu-Sb system and possible suggestion as to why these systems should be different will be taken up in the final chapter of this thesis.
3.6 COPPER - ANTIMONY SYSTEM

Heumann has reported that diffusion in the copper-antimony system was significantly affected by applied stress and the present investigation was carried out in order to extend the previous results. However, as will be seen later, the observations proved to be significantly different from those reported previously.

3.6.1 THE PHASE DIAGRAM

The phase diagram of Cu-Sb is well established and is shown in fig. 53. The temperature of investigation was 390°C, the same as that used by Heumann et al. At this temperature three phases, Cu₄.₅Sb (complex hexagonal), Cu₃Sb (orthorhombic) and Cu₂Sb (tetragonal), are stable. Specific volume calculations show that there are contractions of 12.2 and 9.5 pct when copper and antimony react to form Cu₃Sb and Cu₂Sb respectively and there is an increase of 7.1 pct when the phase Cu₄.₅Sb is formed. These volume changes are large compared to the other systems investigated.

3.6.2 IDENTIFICATION OF THE PHASES

The two phases present in the diffusion zone were identified by microprobe analysis and by X-ray diffraction (Appendix 2). The probe traverse is shown in fig. 54; the compositions of the phases agree well with Cu₂Sb(γ) and Cu₃Sb(κ).

3.6.3 THE EFFECT OF STRESS ON DIFFUSION

The effect of stress on diffusion in Cu-Sb is quite small. Fig. 55 shows the photomicrographs of the diffusion zone obtained by
Fig. 53 Phase diagram of Cu-Sb (Hansen^{70})
Fig. 54 Electron probe traverse of the diffusion zone in Cu-Sb. Specimen annealed for 9 hrs. at 350°C and 50 psi. Probe analysis carried out using Cu-Kα radiation.
Fig. 55 Photomicrographs of the diffusion zone obtained by annealing specimens for 9 hrs. at 390°C at different stresses. 58 x
annealing specimens at 390°C for 9 hours under different stresses. Fig. 56 shows the width of the diffusion zone as a function of stress. The thickness of Cu₃Sb increased with increasing stress up to 400 psi - from 220µ at zero stress to 360µ at 400 psi - whilst the width of Cu₂Sb did not change. The degree of stress sensitivity in Cu-Sb is similar to that observed in Ag-Sb and Ag-Se, although in Cu-Sb two phases are observed in the diffusion zone.

3.6.4 KINETICS

Growth curves at different stresses are shown in fig. 57 and 58. Fig. 57 shows that there is an incubation period for the formation of Cu₃Sb at low stresses; this period decreased linearly with stress, as shown in fig. 59, with no incubation period being observed above 80 psi. It will be recalled that a similar effect has been observed in Cu-Se. At lower stresses, the Cu₂Sb phase grew initially at a fast rate, which slowed down after the appearance of Cu₃Sb, and followed the same curve as the high pressure results. In considering x vs √t plots the time origin for Cu₃Sb is taken as the time at which the phase nucleated, just as in Cu-Se. When the data are plotted in this way the results indicate parabolic growth behaviour for both the phases (fig. 60 and 61). Fig. 62 shows the resultant growth rates of Cu₃Sb and Cu₂Sb as a function of stress. It is observed that the growth rate of Cu₃Sb increases progressively with increasing stress up to 400 psi and above this stress no variation in the growth rate is observed. The growth rate of Cu₂Sb is apparently unaffected by the applied stress.

Tests in which diffusion was allowed to take place at zero stress after an initial high pressure diffusion anneal gave results similar
Fig. 56 Graph showing the width of diffusion zone obtained by a 9 hr. anneal at 390°C as a function of stress
Fig. 57 Growth of Cu$_3$Sb at 390°C at different stresses
Fig. 58  Growth of Cu₂Sb at 390°C at different stresses
Fig. 59 Graph showing incubation period for Cu₃Sb as a function of stress
Fig. 60 Parabolic plot of the growth of Cu₃Sb and Cu₂Sb at 390°C and at 50 psi. Time scale corrected for the incubation period for Cu₃Sb.
Fig. 61 Parabolic plot of the growth of $\text{Cu}_3\text{Sb}$ and $\text{Cu}_2\text{Sb}$ at 390$^\circ$C and 400 psi.
Fig. 62  Growth rates of Cu₃Sb and Cu₂Sb at 390°C as a function of stress
to those in Cu-Se (fig. 63). It was observed that the width of Cu$_3$Sb was reduced and that this phase disappeared after 34 hours whilst the antimony-rich phase, Cu$_2$Sb, grew at the expense of the Cu$_3$Sb, but nevertheless continued to grow even after the disappearance of the Cu$_3$Sb phase.

3.6.5 HYDROSTATIC TESTS

For studying the diffusion under hydrostatic pressure, specimens were prebonded at 390°C for 1 hour under a compressive stress of 400 psi and then diffused under a hydrostatic pressure of 315 psi. The results are shown in fig. 64. It can be seen that the results are very similar to those in Cu-Se. The Cu$_3$Sb phase grew initially for a short length of time (10 hours) after which its thickness decreased. The Cu$_2$Sb phase, however, grew with increasing heating time, initially at a slower rate, but the growth rate increased when Cu$_3$Sb started to regress. The results are similar to the experiments carried out at zero stress after an initial high pressure anneal indicating that hydrostatic pressure is of no significance in the diffusion characteristics of this system.

3.6.6 KIRKENDALL TESTS

A photomicrograph of a typical Kirkendall marker experiment is shown in fig. 65. The markers stayed on the Cu$_3$Sb/Cu interface indicating that copper is the diffusing species. Ledges of copper are observed under the tungsten markers, characteristic of a pressure sensitive diffusion process.

A fairly detailed examination of the Kirkendall effect was
Fig. 63 Graph showing the shrinkage of Cu$_3$Sb and growth of Cu$_2$Sb when initial stress of 400 psi is released after 16 hours and diffusion proceeds at zero stress. Results for growth of Cu$_3$Sb and Cu$_2$Sb at 400 psi and zero psi are provided for comparison.
Fig. 64 Growth of Cu$_3$Sb and Cu$_2$Sb, annealed at 390°C under hydrostatic pressure of 315 psi. Normal growth curves at 400 psi and zero psi are shown for comparison.


**Fig. 65** Micrograph of Kirkendall experiment. Specimen annealed for 50 hrs. at $390^\circ C$ and 1000 psi. 30 x
carried out in this system similar to the tests made in Ag-Sb (page 54).

Fig. 66 shows Kirkendall marker experiments carried out for 0,1 and 2 1/2 hours. Initially the markers act as barriers to diffusion and the width of the diffusion zone is zero at the marker position with ledges of both silver and antimony on either side of the markers. As diffusion proceeds, lateral diffusion takes place and the Cu2Sb/Sb boundary is smoothed out quickly. The copper ledge at the Cu/Cu3Sb boundary is maintained for a long time since diffusion of copper into Cu3Sb in the lateral direction is restricted due to the absence of applied pressure. Fig. 67 shows a marker experiment using different size markers. The height of the copper ledge increased with increasing marker size due to the increasing amount of lateral diffusion required. The results in Cu-Sb are, therefore, very similar to those in Ag-Sb indicating that the presence of two phases in the diffusion zone is of no significance to the mode of development of the ledges.

3.6.7 DISCUSSION

The stress effect in Cu3Sb is similar to that in Ag-Sb and Ag-Se and has its origin in the elimination of the Kirkendall porosity at the Cu/Cu3Sb interface. The growth of Cu2Sb is unaffected by pressure as might be expected since the growth of this phase depends on the copper flux across and out of the Cu3Sb phase, i.e. on the concentration gradient in Cu3Sb, and this did not change very much with pressure.

At low stresses, a nucleation effect is observed in Cu-Sb which is fairly similar to but smaller than that observed in Cu-Se. There is a nucleation time required for the formation of Cu3Sb and this time decreased as the applied pressure increased. The Cu2Sb had a slightly faster growth
Fig. 66 Photomicrographs of Kirkendall experiments in Cu-Sb annealed at 390°C for various times at 1000 psi
Fig. 67 Photomicrograph of the Kirkendall experiment in Cu-Sb diffused at 390° C for 50 hrs. under 1000 psi with different size markers 21 x
rate before Cu$_3$Sb nucleated than when both phases were present. However, the flux of copper atoms into the diffusion zone increases markedly when Cu$_3$Sb nucleates, indicating that the initial interface formed is defective, although not as poor as in the Cu-Se system.

The Cu-Sb system shows a tendency for the formation of a poor interface between copper and the diffusion zone just as in Cu-Se. This is evidenced by the nucleation time at the beginning of diffusion discussed above, and by tests in which the pressure was suddenly released in the middle of the diffusion anneal and the Cu$_3$Sb phase started to shrink. This effect was observed in two of the five systems investigated and possible explanations are discussed in the next chapter.

The stress effect in Cu-Sb observed in the present investigation is significantly different from that reported by Heumann et. al.$^{4,5}$ (see page 4). They found that even at high stresses there was still a significant nucleation time for the formation of Cu$_3$Sb (e.g. 1 hour at 850 psi, see Fig. 68).

![Graph](image)

**Fig. 68** Growth of Cu$_2$Sb and Cu$_3$Sb at 390°C and 850 psi$^2$ (Heumann et. al.$^4$)
In the present work Cu$_3$Sb was found to be present after 4 hours anneal at zero stress and above 80 psi it appeared from the beginning of diffusion. It is difficult to account for such a large discrepancy between the two sets of data which were apparently obtained under similar experimental conditions. Heumann has also reported that the growth of Cu$_3$Sb occurred in three stages, with a fast growth stage apparently superimposed between two slower rates. It is very difficult indeed to give any explanation for such a growth curve, and it may well be that Heumann is putting too much weight on the accuracy of two experimental points. However, the growth rate at longer time ($11.5 \times 10^{-5}$ cm/√sec.) is in good agreement with the growth rate at zero stress ($11.3 \times 10^{-5}$ cm/√sec.) in the present investigation.

Heumann also carried out a set of experiments in which the pressure was suddenly changed during the course of a diffusion anneal. From these experiments it was concluded that below a critical pressure of 570 psi, Cu$_3$Sb did not appear in the diffusion zone. These results are similar to the results obtained in the present investigation, although the magnitude of stress involved was very much greater in Heumann's work.

The discrepancies between the results of Heumann et. al. and the present investigation are possibly due to the friction between the specimen and the die walls in Heumann's apparatus, whereas the stress is purely compressive in the present investigation with no possibility of friction affecting the results in any way. If such friction is involved the applied stress would not be a true measure of the pressure applied to the diffusion couple.
CHAPTER IV
SUMMARY AND CONCLUSIONS

In previous chapters, it has been suggested that the effect of stress on diffusion is due to the elimination of the Kirkendall porosity thereby increasing the surface area for diffusion and thus the atomic flux. It has also been stated that variations in the diffusion coefficient and phase boundary compositions are not significant in the stress range used in the experiments. In the following section attempts will be made to obtain a quantitative measure of these effects and their relative significance.

4.1. RELATIVE VARIATIONS OF DIFFUSION COEFFICIENT AND PHASE BOUNDARY COMPOSITION

Castleman has shown that the relative effect of variations of the diffusion coefficient and phase boundary compositions with pressure depend on the factor \( \mu \), given in eq. (1.21) (see page 29). He suggested that a pressure induced change in the interface concentration would not be important unless the factor '\( \mu \) has a value, say, greater than fifty. This factor has been calculated for the Ag-Sb and Ag-Se system and is given in Table 5. Eq. (1.21) has been derived on the assumption that the growth rates of the two interfaces of the diffusion zone are equal and opposite, and it is not completely accurate when applied to Ag\(_3\)Sb and Ag\(_2\)Se. The '\( \mu \)' factors calculated will therefore be approximate. However, the values are very small, being less than two for both Ag\(_3\)Sb and Ag\(_2\)Se, suggesting that the change in phase boundary composition is insignificant in comparison with apparent changes in the diffusion coefficient. These calculations could not be extended to the Cu-Se, Cu-Sb and Ni-Sb systems since more than one phase was present in the diffusion zone and so Castleman's theory cannot be used. However, it seems reasonable that in these systems
as well, the variation in phase boundary composition is negligible compared with the variation in the diffusion coefficient.

4.2 EFFECT OF PRESSURE ON DIFFUSION COEFFICIENT

It has been shown in page 22 that diffusion coefficients generally decrease with pressure as represented by eq. (1.16). There is insufficient data on activation volumes to calculate accurately the effect of pressure on diffusion coefficients in the systems investigated in this work. However, estimates can be made by assuming that the activation volumes for formation and for migration of vacancies are equal and that both are equivalent to the atomic volume of the diffusing species. These assumptions will yield an upper limit for the variation in diffusion coefficients with pressure since the relaxation of atoms around a vacancy have been ignored\textsuperscript{83}.

In Ag\textsubscript{2}Se and Cu\textsubscript{2}Se, the sum of the covalent radii of the species (2.69\textdegree for Ag\textsubscript{2}Se and 2.54\textdegree for Cu\textsubscript{2}Se) are in reasonably good agreement with the nearest neighbour distance (2.16\textdegree for Ag\textsubscript{2}Se and 2.54\textdegree for Cu\textsubscript{2}Se) calculated from a knowledge of the CaF\textsubscript{2} type structure and the lattice parameter. Hence Ag\textsubscript{2}Se and Cu\textsubscript{2}Se are considered to have essentially covalent bonding and the atomic volumes of Ag and Cu were calculated from their respective covalent radii. In Ag\textsubscript{3}Sb and Cu\textsubscript{3}Sb, the bonding is essentially metallic and the atomic diameters of Cu and Ag were taken to be representative of the diffusing species\textsuperscript{84}. Using these values the ratio of the diffusion coefficient at 1000 psi to that at zero pressure was calculated at the temperature of the experiment and the results presented in Table 5. It is seen that the diffusion coefficients decrease by less than
<table>
<thead>
<tr>
<th>Phase</th>
<th>Growth rate in cm/√sec.</th>
<th>Temp.</th>
<th>μ</th>
<th>Activation volume for diffusion</th>
<th>$\frac{D(P)}{D(o)}$ at 1000 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}_3\text{Sb}$</td>
<td>$13.7 \times 10^{-5}$</td>
<td>$350^\circ\text{C}$</td>
<td>1.47</td>
<td>$11.9 \ \text{Å}^3$</td>
<td>97.7%</td>
</tr>
<tr>
<td>$\text{Ag}_2\text{Se}$</td>
<td>$14.8 \times 10^{-5}$</td>
<td>$130^\circ\text{C}$</td>
<td>2.02</td>
<td>$30.0 \ \text{Å}^3$</td>
<td>91.6%</td>
</tr>
<tr>
<td>$\text{Cu}_2\text{Se}$</td>
<td>$22.4 \times 10^{-5}$</td>
<td>$170^\circ\text{C}$</td>
<td>-</td>
<td>$22.0 \ \text{Å}^3$</td>
<td>96.5%</td>
</tr>
<tr>
<td>$\text{Cu}_3\text{Sb}$</td>
<td>$18.3 \times 10^{-5}$</td>
<td>$390^\circ\text{C}$</td>
<td>-</td>
<td>$17.12 \ \text{Å}^3$</td>
<td>97.0%</td>
</tr>
</tbody>
</table>
10 pct for all the phases at 1000 psi whereas the experimentally observed increase in growth rates of all these phases with stress suggests a large increase in the diffusion coefficients. The significant decrease in the diffusion coefficient in Ag₂Se at 1000 psi is due to the large value of the activation volume assumed in the calculation. In known cases (Cu⁸⁵, Au⁸⁶), the activation volumes are of the order of half the atomic volume and this would make the effect much less. However, it can be concluded that the stress sensitivity observed in this work is not due to changes in the phase boundary composition or in the diffusion coefficient. Other experimental evidence supports this conclusion. In Ag-Sb, Ag-Se and Cu-Sb there is a maximum growth rate above a certain limiting stress rather than the continuously varying rate which would be expected from variations in phase boundary composition and diffusion coefficient. Furthermore, tests in Ag-Sb show that hydrostatic pressure does not have any influence on growth rates, whereas for variations in the equilibrium composition and diffusion coefficient hydrostatic pressure should have an effect very similar to that of compressive stress.

4.3 EFFECT OF STRESS ON THE KIRKENDALL POROSITY

As discussed in the previous chapter the results of the experiments can be explained very satisfactorily in terms of the Kirkendall porosity. In multiphase systems showing a large Kirkendall effect, there will be a large vacancy flux equal and opposite to the atomic flux. These vacancies can condense on one side of the diffusion zone, at the interface between the diffusing species and the diffusion zone, to form voids. This would decrease the effective surface area for diffusion, thus reducing the flux of atoms into the diffusion zone. Application of stress
will improve the interface by reducing the Kirkendall porosity, thus increasing the atomic flux into the diffusion zone and so increasing the growth rate. However, once the applied stress is sufficiently great to give unrestricted flux, no effect of stress will be observed as seen in Ag-Sb, Ag-Se and Cu-Sb. The thicknesses of Cu$_2$Se and Ni$_2$Sb$_2$ (and Cu$_2$Te in the work of Brown et. al.$^6$) appeared to increase linearly with the applied stress and no limiting stress was observed above which the growth rates were constant. This is probably because the diffusion coefficients in these phases are very large, much higher than in any of the other thermally stable phases. In Cu$_2$Se, for example, the chemical inter-diffusion coefficient of copper has been reported$^{89}$ to be $2.45 \times 10^{-4}$ cm$^2$/sec. at 170°C, which is about three orders of magnitude larger than other systems investigated. These systems therefore tend to have a large vacancy flux and a high pressure will be necessary to establish a good interface. The maximum stress of 1500 psi applied in these systems is presumably insufficient to attain these limiting conditions.

In multiphase systems the Kirkendall porosity develops at a single interface of the diffusion zone and it is difficult to determine the pore density by direct observation. However, an estimate of the porosity in Ag-Sb and Ag-Se can be made, assuming that the width of the intermediate phase is proportional to the effective interface area. Beyond the limiting stress, the total interface area of the expecimen is effective and hence:

$$\frac{A}{A_c} = \frac{x}{x_c}$$  \hspace{1cm} (1.24)

where $A = $ effective interface area at pressure $P$.

$A_c = $ cross-sectional area of the specimen.

$x = $ width of the diffusion zone at stress $P$.

$x_c = $ width of the diffusion zone above the limiting stress.
Eq. (1.24) gives an effective area of 61.0 pct and 31.0 pct for Ag-Sb and Ag-Se respectively, at the zero stress. Barnes and Mazey have found that the average void radius at the zero stress is $5 \times 10^{-4}$ cm in Cu-Ni and that there are $6.4 \times 10^5$ voids/cm$^2$ in the region of maximum porosity. If the void radius is assumed to be the same in the present work Ag-Sb gives $4.9 \times 10^5$ voids/cm$^2$ and Ag-Se $8.1 \times 10^5$ voids/cm$^2$ at zero stress, these values being of the same order of magnitude as in the Cu-Ni system.

As discussed in page 40, no stress effect was observed in the Cu-Zn, Cu-Sn, and Al-Zr systems (at stresses up to 1500 psi). These systems show a small Kirkendall effect compared with the systems investigated in detail in this thesis. The vacancy flux is thus smaller and porosity would be developed over a significant volume of the diffusion zone rather than just at an interface. Hence, the effective surface area of diffusion is not affected significantly by the Kirkendall porosity. It therefore appears that the stress effect is significant only in systems with a large Kirkendall effect.

There seems little doubt that the effect of stress is to reduce the amount of porosity so that the vacancies are now removed exclusively by dislocation movement. The details of the mechanism by which this occurs are somewhat uncertain, however, and it is not possible to say whether the effect is thermodynamic or mechanical in origin.

It has been shown that growth rates are not affected by hydrostatic pressure and that only compressive loading is effective in preventing Kirkendall porosity. This would tend to indicate that the
reduction in porosity is mechanical in origin with any pores tending to form being compressed in the direction of diffusion and so prevented from developing. The compression could take place by a micro-creep process around the incipient pore, although it should be emphasised that no detectable creep was observed in any of the systems examined and the temperatures and pressures used in this work were very low for any creep.

Barnes and Mazey\(^\text{36}\) found that when pressure is applied to a single phase diffusion couple containing pores, the pores shrink but maintain their spherical shape. This would indicate that the effect of pressure is to render the pores thermodynamically unstable. In the present system, it may well be that the stress prevents nucleation of the pores since an extra energy term is now involved in their formation (see page 31). However, it is difficult to see how pressures as low as 50 psi should be sufficient for this.

4.4 GROWTH KINETICS

All systems investigated in this work showed a parabolic growth for all phases over the complete stress range investigated. In Cu-Sb and Cu-Se there was an incubation period at low stress levels before normal growth took place. However, once this effect was accounted for, these systems, likewise, showed a parabolic growth.

The fact that parabolic growth is always observed indicates that the restriction to growth at low pressures has its origin in a diffusion process. This restriction to growth appears to occur at a phase boundary. However, it is not a normal example of an interface controlled process which would ordinarily give a linear growth rate. Rather, the development of
the Kirkendall porosity causes a physical reduction in the interface area and so a decrease in the growth rate.

Experiments in which diffusion was allowed to take place at low stress after an initial high stress diffusion anneal showed two different characteristics depending on the system investigated. In Ag-Sb and Ni-Sb, growth continued for a short time at a rate characteristic of the initial high pressure. Eventually, however, the growth rates decreased and assumed the rates characteristic of the new stress. This transient effect is expected since a finite time is necessary for the development of the degree of the Kirkendall porosity characteristic of the new pressure. During this time the good bond developed at high pressure will be retained. Results of similar experiments in Cu-Se and Cu-Sb produced growth rates much slower than expected, and these will be discussed in a later section.

All the stress sensitive systems were found to have a large Kirkendall effect. Ledges were invariably found adjacent to the tungsten markers. This effect was much greater than in non-pressure-sensitive systems and was attributed to the absence of stress in the lateral direction of diffusion, thus giving restricted atomic flux in this direction.

The nature of results obtained here allows the results of Brown et. al. on diffusion in Cu-Te to be interpreted somewhat better. There seems little doubt now that growth of Cu$_2$Te at high pressure is strictly parabolic and the apparent deviation from the parabolic growth found by Brown et. al. is due to the significant scatter in their experimental results. In the experiments at zero stress following a high pressure anneal (fig. 3 (b) page 7), the experimental data at short times was neglected. If this data is incorporated in the plot, a
 transient period can be seen to precede the regression of Cu$_2$Te just as have been found in Ag-Sb and Ni-Sb.

Although experiments at different temperatures were not carried out in all the systems, the results of Ag-Sb and Cu-Te$^6$ show that pressure sensitivity is not characteristic of a particular temperature and that the nature of the variation of the growth rate with pressure remains essentially the same. However, the degree of variation may change with temperature.

4.5 RESTRICTED DIFFUSION IN Cu-Sb AND Cu-Se

The Cu-Sb and Cu-Se systems showed a tendency for a restricted atom transfer from the copper into the diffusion zone under certain circumstances. This occurred at the beginning of diffusion under low stresses when there was a nucleation time for the Cu$_3$Sb and Cu$_2$Se phases. In tests in which diffusion was allowed to take place at a low stress after an initial high stress anneal, there was again a very small copper flux into the diffusion zone and this led to the gradual disappearance of the Cu-rich phases in both systems. In this section various possibilities are explored to explain the results.

Table 6 lists values of energy of formation (where available) for the stable compounds in the various alloy systems studied. Baird$^{39}$ has suggested that in Cu-Sb, the diffusion temperature ($390^\circ$C) is only $15^\circ$ above the temperature at which Cu$_3$Sb decomposes by a eutectoid reaction, so that the free energy reduction on forming Cu$_3$Sb from the adjoining phases at $390^\circ$C must be small and therefore a finite nucleation time would be expected, since the driving force to form the nucleus will be small.
TABLE 6

ENERGY OF FORMATION, CRYSTAL STRUCTURE AND SPECIFIC VOLUME CHANGES FOR INTERMETALLIC PHASES

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal Structure</th>
<th>Heat of Formation at 298°K, kcal/mol.</th>
<th>Entropy of Formation at 298°K, cal/mol/deg.</th>
<th>Change in Specific Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₃Sb</td>
<td>Orthorhomic (Cu₃Ti type)</td>
<td>-5.5 ± 1.5</td>
<td>41.0 ± 3.0</td>
<td>-6.11</td>
</tr>
<tr>
<td>ζ (Ag-Sb)</td>
<td>h.c.p.</td>
<td>-</td>
<td></td>
<td>-0.43</td>
</tr>
<tr>
<td>Ag₂Se</td>
<td>F.C.C. (CaF₂ type)</td>
<td>-10.3 ± 0.2</td>
<td>35.9 ± 0.1</td>
<td>+3.23</td>
</tr>
<tr>
<td>Ni₁₅Sb</td>
<td>Superstructure of cubic</td>
<td>-</td>
<td></td>
<td>-8.4</td>
</tr>
<tr>
<td>Ni₃Sb</td>
<td>?</td>
<td>-</td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>Ni₅Sb₂</td>
<td>Tetragonal</td>
<td>-36.4 ± 2.5</td>
<td>-</td>
<td>-0.03</td>
</tr>
<tr>
<td>NiSb</td>
<td>Hexagonal</td>
<td>-15.5 ± 1.0</td>
<td>-</td>
<td>-3.64</td>
</tr>
<tr>
<td>NiSb₂</td>
<td>Orthorhombic</td>
<td>-17.7 ± 1.0</td>
<td>-</td>
<td>-11.2 (?)</td>
</tr>
<tr>
<td>Cu₂Se</td>
<td>F.C.C. (CaF₂ type)</td>
<td>-14.2 ± 0.2</td>
<td>-</td>
<td>+0.4</td>
</tr>
<tr>
<td>Cu₃Se₂</td>
<td>Orthorhombic</td>
<td>-23.65 ± 1.0</td>
<td>-</td>
<td>-5.2</td>
</tr>
<tr>
<td>CuSe</td>
<td>Hexagonal</td>
<td>-9.45 ± 0.5</td>
<td>22.5 ± 1.5</td>
<td>+0.99</td>
</tr>
<tr>
<td>Cu₄.₅Sb</td>
<td>h.c.p.</td>
<td>-</td>
<td></td>
<td>+7.07</td>
</tr>
<tr>
<td>Cu₃Sb</td>
<td>Orthorhombic (Cu₃Ti type)</td>
<td>-</td>
<td></td>
<td>-12.4</td>
</tr>
<tr>
<td>Cu₂Sb</td>
<td>Tetragonal</td>
<td>-3.0 ± 0.4</td>
<td>24.25 ± 0.8</td>
<td>-9.5</td>
</tr>
</tbody>
</table>

* Pressure sensitive phases
However, the small range of stress in which delayed nucleation is observed would not alter the free energy of the system significantly and it would appear that this suggestion is not correct. Actual values of energy of formation are not available in Cu-Sb. However, heats of formation are available for the pressure sensitive phases in Cu-Se, and it can be seen that these values are quite large, being higher than for pressure sensitive phases in Ag-Sb and Ag-Se but less than for Ni$_5$Sb$_2$. Hence the restricted diffusion in Cu-Sb and Cu-Se is not related to the energy of formation of the phases.

Baird$^{39}$ has also suggested that delayed nucleation may be caused by a poor contact between the mating surfaces of the diffusion couple or by the presence of an oxide layer at the interface. Application of stress would improve the interface by producing better contact between the surfaces or by fracturing the oxide layer, thus decreasing the time for the start of normal diffusion. These suggestions may be applicable, to some extent, to nucleation effects at the beginning of diffusion. However, they fail to explain the restricted diffusion which occurs when the stress is suddenly removed from a couple which was allowed to diffuse at a higher stress previously. Here, good contact has already been established and there is no possibility of an oxide layer interfering with diffusion. In any case, these suggestions do not explain why there is poor mating or an oxide film in Cu-Sb and Cu-Se but not in the other systems investigated.

Table 6 shows that there is a large contraction in volume involved in forming Cu$_3$Sb (-12.2 pct). This would certainly make it difficult to nucleate the phase at a low pressure. Furthermore, in the course of a diffusion anneal, a high stress will be generated at the Cu/Cu$_3$Sb interface.
This stress would make the interface very fragile and any shock or change in the diffusion conditions would cause it to crack. Varying the stress in the middle of a diffusion anneal could cause such a crack to develop and so would give very restricted atom transfer across the interface. This suggestion has many attractive features as it would explain why the effect was not observed in the Ag-Sb, Ag-Se and Ni-Sb systems, since in these systems the phases formed with much smaller changes in specific volume than in Cu-Sb. However, it has the major drawback that it cannot possibly explain the results in Cu-Se since Cu$_2$Se apparently forms with 0.4 pct increase in volume.

Hence, it has not been possible to find any explanation which can adequately account for all aspects of the restricted diffusion in Cu-Sb and Cu-Se. There seems some merit in the suggestion that the effect is caused by a decrease in the specific volume in the pressure sensitive phase although it cannot adequately explain all the experimental results. It would be very interesting to find other systems which show this restricted diffusion effect as this might help to find the underlying cause.

4.6 DIFFUSION COEFFICIENTS AND NON-APPEARANCE OF THE STABLE PHASES

Diffusion coefficients for the intermetallic phases were estimated from the growth rate data, assuming a linear composition profile using the method discussed in the Introduction (page 19). Values are listed in Table 7. It is observed that the diffusion coefficients are generally about two orders of magnitude greater than the growth constants. The diffusion coefficients for Cu$_3$Sb and Cu$_2$Sb calculated from the present data are in good agreement with those reported by Heumann et. al.$^{4,5}$. 
<table>
<thead>
<tr>
<th>System</th>
<th>Intermetallic phases</th>
<th>Temp.</th>
<th>Composition range</th>
<th>Rate Constant α in cm/√sec.</th>
<th>'D' calculated cm²/sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Sb</td>
<td>Ag₃Sb</td>
<td>350°C</td>
<td>73.6 - 78.6 at % Ag</td>
<td>13.7 x 10⁻⁵</td>
<td>2.98 x 10⁻⁸</td>
</tr>
<tr>
<td>Ag-Se</td>
<td>Ag₂Se</td>
<td>170°C</td>
<td>66.7 - 67.3 at % Ag</td>
<td>14.8 x 10⁻⁵</td>
<td>1.34 x 10⁻⁷</td>
</tr>
<tr>
<td>Cu-Sb</td>
<td>Cu₃Sb</td>
<td>390°C</td>
<td>77.7 - 79.2 at % Cu</td>
<td>18.3 x 10⁻⁵</td>
<td>1.1 x 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>Cu₂Sb</td>
<td>390°C</td>
<td>65.4 - 67.7 at % Cu</td>
<td>7.2 x 10⁻⁵</td>
<td>7.8 x 10⁻⁷</td>
</tr>
</tbody>
</table>

* Heumann's results

*4*
The diffusion coefficients for Ni$_5$Sb$_2$ and Cu$_2$Se cannot be calculated since there is no limiting stress above which the growth rate is constant. However, as discussed in section (4.3) the diffusion coefficient in Cu$_2$Se at 170°C is $2.45 \times 10^{-4}$ cm$^2$/sec. which is much higher than the diffusion coefficients calculated for other systems.

In the systems studied, some of the stable phases predicted from the phase diagram were not observed in the diffusion zone, for example $\zeta$ in Ag-Sb; Ni$_{7.5}$Sb, NiSb$_2$ in Ni-Sb; CuSe in Cu-Se; and Cu$_{4.5}$Sb in Cu-Sb. Similar observations have also been made in Ni-Al$^8$ and U-Al$^3$. Non-appearance of these phases even after the application of a high stress suggests that they are not sensitive to applied stress and that their non-appearance is a true growth effect. Castleman and Froot$^{90}$, investigating Ni-Al, suggested that the absence of NiAl and Ni$_3$Al in the diffusion zone was due to their smaller growth rates compared to the other phases. In the Cu-Sb system, Cu$_{4.5}$Sb has a diffusion coefficient of $\sim 10^{-9}$ cm$^2$/sec.$^4$ which is about two orders of magnitude less than that of Cu$_3$Sb ($\sim 10^{-7}$ cm$^2$/sec.) and Cu$_2$Sb ($\sim 10^{-7}$ cm$^2$/sec.) Hence its growth rate will be very small and it would not be observed in the diffusion zone. The diffusion coefficients for phases in other systems are not available for a quantitative comparison; however, the same explanation probably will also hold true for them.
1. The growth of the intermetallic phases in all systems investigated is parabolic and hence controlled by diffusion.

2. The effect of stress is to increase the growth rates of the stress sensitive phases by decreasing the amount of the Kirkendall porosity developed during diffusion and thus increasing the cross-section of diffusion. The stress sensitive phase is generally the one adjacent to the pure metal providing the diffusing atoms.

3. In those systems in which the pressure sensitive phase has a very large intrinsic growth rate, this rate increases linearly with stress, whereas in other systems there is a limiting stress above which there is no variation in growth rates, the limiting stress corresponding to the absence of the Kirkendall porosity.

4. The stress effect is observed at different temperatures and is not characteristic of any particular temperature.

5. In systems showing delayed nucleation the nucleation time decreases linearly with stress.

6. Hydrostatic pressure has no significant effect on the growth rates of the intermetallic phases and the results do not correspond to the effect observed under compressive stress of the same magnitude.

7. It is a necessary condition for stress sensitive systems to have a large Kirkendall effect and the presence of ledges under the markers is characteristic of these systems.
APPENDIX I

X-RAY DIFFRACTION ANALYSIS OF INTERMEDIATE PHASES
Table Al  X-Ray Analysis of Ag₃Sb Phase

<table>
<thead>
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<th>d in Å</th>
<th>( \frac{I}{I_0} )</th>
<th>d in Å</th>
<th>( \frac{I}{I_0} )</th>
</tr>
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<td>d in Å</td>
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Table A3. X-Ray Analysis of Cu₃Se₂

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<th>d in Å</th>
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### Table A4. X-Ray Analysis of Cu₃Sb Phase

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APPENDIX II

Growth Kinetics in Cu-Se and Cu-Sb
Fig. II-1  Growth of Cu$_2$Se and Cu$_3$Se$_2$ at 170°C and 100 psi

Cu-Se
t$_0$ = 3.75 hrs. for Cu$_2$Se

Cu$_3$Se$_2$

Fig. II-2  Growth of Cu$_2$Se and Cu$_3$Se$_2$ at 170°C and 200 psi
**Fig. II-3** Growth of Cu$_2$Se and Cu$_3$Se$_2$ at 170°C and 300 psi

**Cu-Se**

$t_0 = 3.0$ hr. for Cu$_2$Se

**Fig. II-4** Growth of Cu$_2$Se and Cu$_3$Se$_2$ at 170°C and 400 psi

**Cu-Se**

$t_0 = 2.0$ hrs. for Cu$_2$Se
**Fig. II-5** Growth of Cu₂Se and Cu₃Se₂ at 170°C and 500 psi

**Fig. II-6** Growth of Cu₂Se and Cu₃Se₂ at 170°C and 1500 psi
Fig. II-7  Growth of Cu$_2$Sb and Cu$_3$Sb at 390°C and zero stress

Fig. II-8  Growth of Cu$_2$Sb and Cu$_3$Sb at 390°C and 100 psi
Fig. II-9  Growth of Cu₂Sb and Cu₃Sb at 390°C and 200 psi

Fig. II-10  Growth of Cu₂Sb and Cu₃Sb at 390°C and 300 psi


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